GenX and other Poly and Perfluoroalkyl Substances (PFAS) in Surface and Drinking Water

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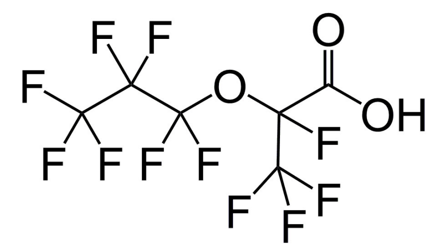


GenX

The Ohio Water Resources Center
Environmental Professionals Network
Water Management Association of Ohio
Environmental Professionals Network
Tuesday, March 5, 2019

Overview

- GenX and other PFAS in the Cape Fear River, drinking water, update on what we know, discussion of contributing factors

- Introduction to PFAS, chemistry, consumer and industrial uses

- Summary of research in the Cape Fear River Basin

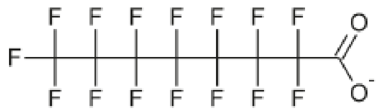
- Discussion of Non-targeted Analysis Mass Spectrometry techniques

- Reductions in PFAS in municipal drinking water, but still many unresolved issues (e.g., well and groundwater contamination, airborne releases, soil, food)

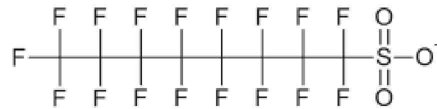
Introduction to PFAS

- A class of man-made chemicals that are ubiquitous due to:
  - Wide variety of industrial and consumer uses
  - Persistence
  - High Mobility
- They are a concern due to:
  - Known or suspected toxicity, especially for PFOS and PFOA
  - Bioaccumulation
  - Some have very long half lives (several years), especially in humans
  - Shorter PFAS tend to be highly mobile, longer PFAS less mobile
- Information on PFAS is rapidly evolving

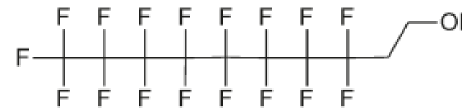
Some Perfluorinated Compounds (PFCs)



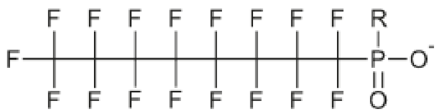
Perfluorocarboxylic acids
(ex. PFOA)



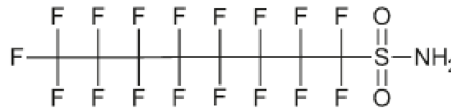
Perfluorosulfonic acids
(ex. PFOS)



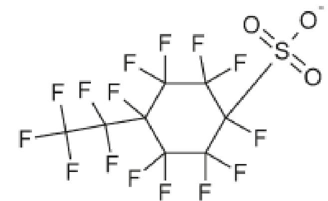
Fluorotelomer alcohol
(ex. 8:2 FTOH)



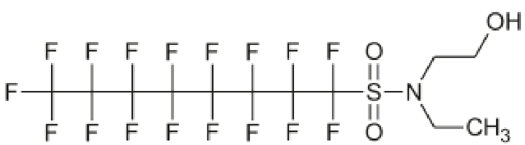
Perfluorophosphonic/phosphinic acids
(ex. If R=OH then PFOPA
If R=C8 perfluoroalkane then 8:8 PFPi)



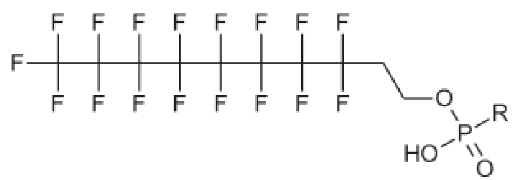
Perfluorosulfonamide
(ex. FOSA)



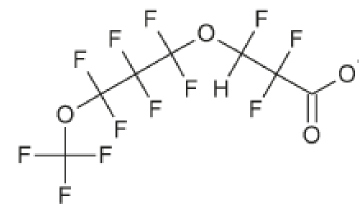
Perfluorinated cyclo sulfonates
(ex. PFECHS)



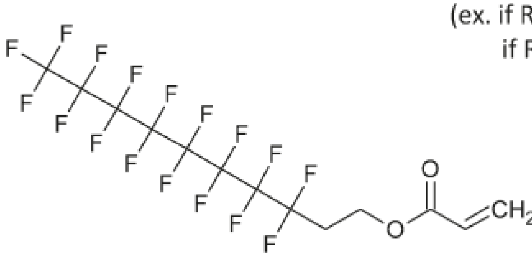
Perfluorosulfonamidoethanol
(ex. N-EtFOSE)



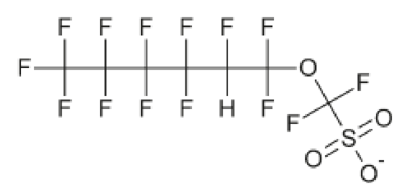
Fluorotelomer phosphate esters
(ex. if R= OH then 8:2 monoPAP
if R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated ether carboxylates
(ex. 4,8-dioxa-3H-perfluorononanoate)



Polyfluorinated polymeric unit
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)



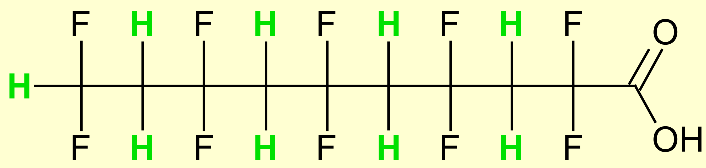
Polyfluorinated ether sulfonates
(ex. Perfluoro [hexyl ethyl ether sulfonate])

Figure 1. Generic structures for polyfluorinated compounds. The $n = 8$ linear carbon structures are shown for many of these examples, but $n = 4-14$ linear and/or branched carbon units are generally possible.

Per- and Polyfluoroalkyl Substances (PFAS) Chemistry 101

Thousands of PFASs in production of industrial and consumer products.

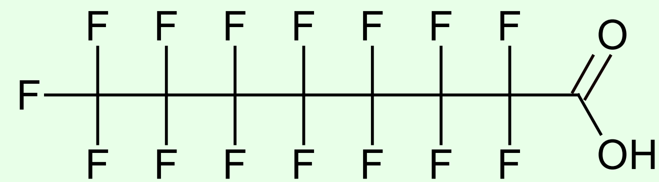
<u>*Poly*</u> fluorinated = many fluorines



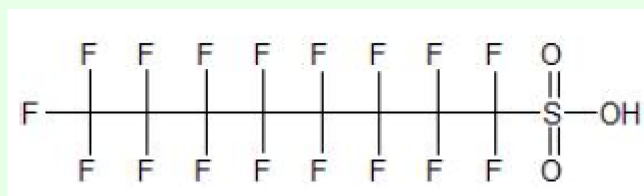
Polyfluorinated carboxylic acid from the production of polyvinylidene fluoride (PVDF) plastic

Newton et al., 2017. Novel polyfluorinated compounds identified downstream of manufacturing facilities near Decatur, AL using high resolution mass spectrometry

<u>*Per*</u> fluorinated = fully fluorinated



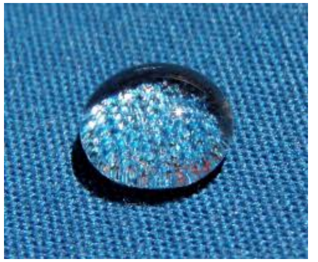
Perfluorooctanoic acid (PFOA ,C-8)



Perfluorooctanesulfonate (PFOS)

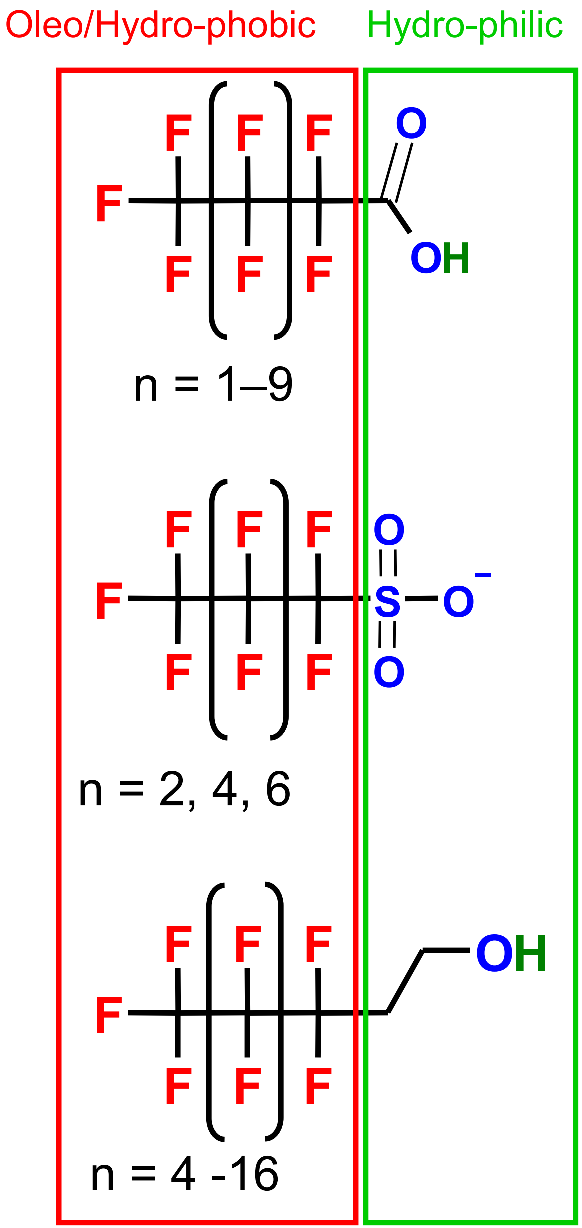
Very stable (C-F bond energy 485 kJ/mol)
(C-C 346, C-N 305, C-O 358, C-Cl 327 kJ/mol)

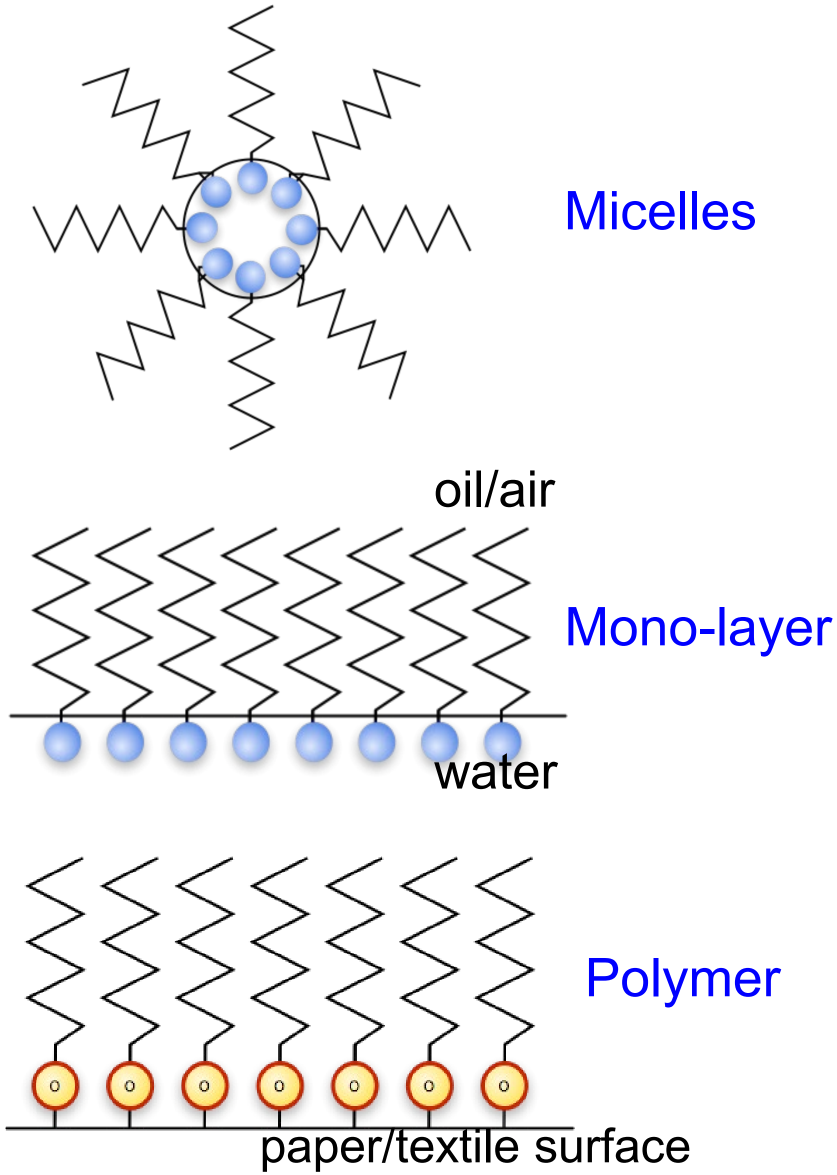
Chemical and Physical Properties



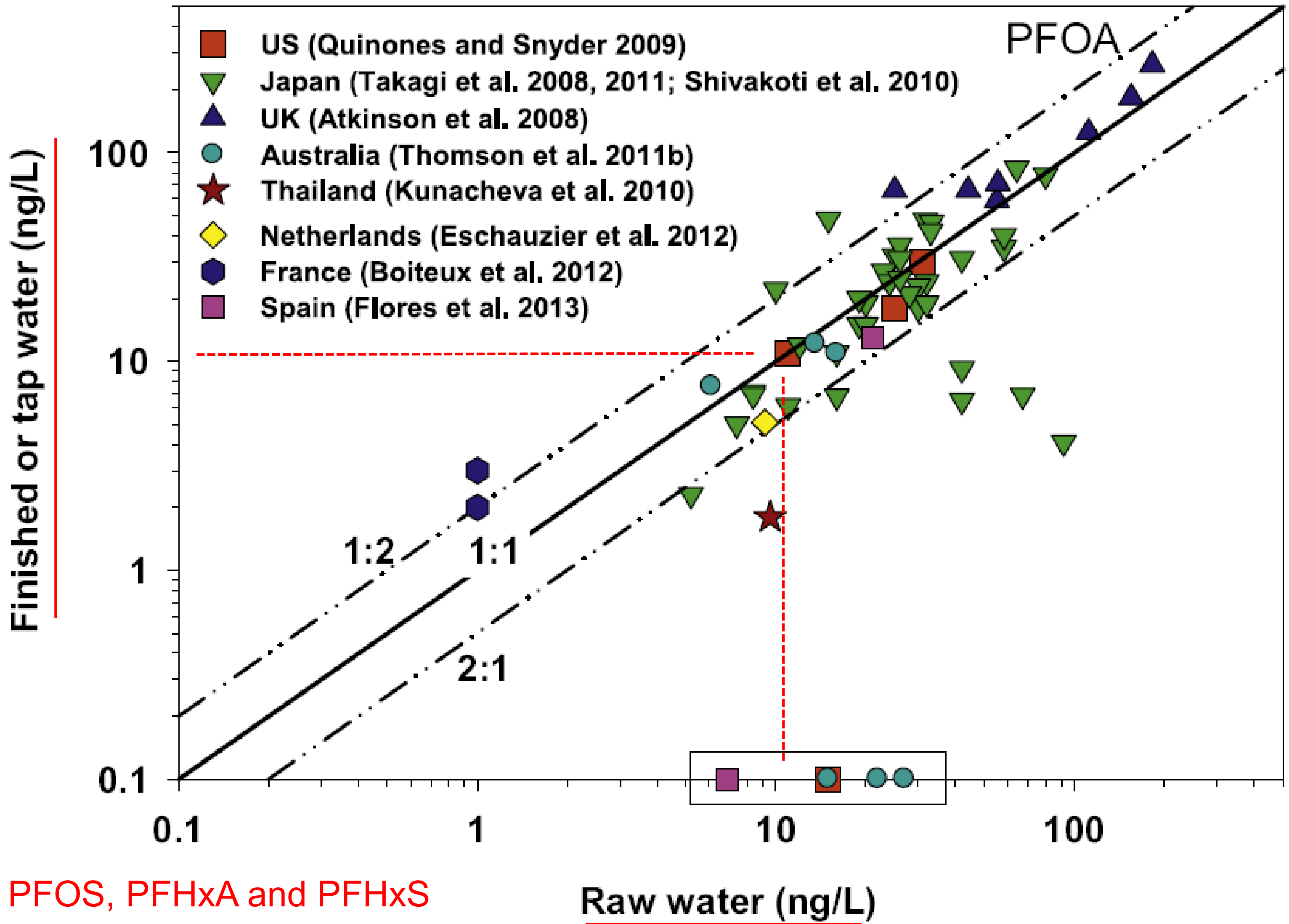
- Properties of PFAS range depending on carbon chain lengths and functional groups.
- PFAS generally occur as mixtures and are not well characterized.
- PFAS provide desirable performance because they repel both oil and water:
  - The fluorinated carbon tail is both lipophobic/oleophobic (repelled by fats and oils) and hydrophobic (repelled by water).
  - The functional group head can vary but is often hydrophilic (attracted to water).
- As a result of these unique surfactant properties and their stability, they are common surfactants and stain preventers.

Surfactant Characteristics of PFAS





PFAS Generally Not Removed During Drinking Water Treatment



Similar for PFOS, PFHxA and PFHxS

Rahman et al., (2014) *Water Research,* 50:318-340

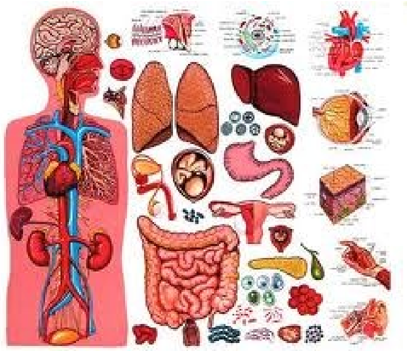
PFAS Health Effects Summary

Animal toxicity

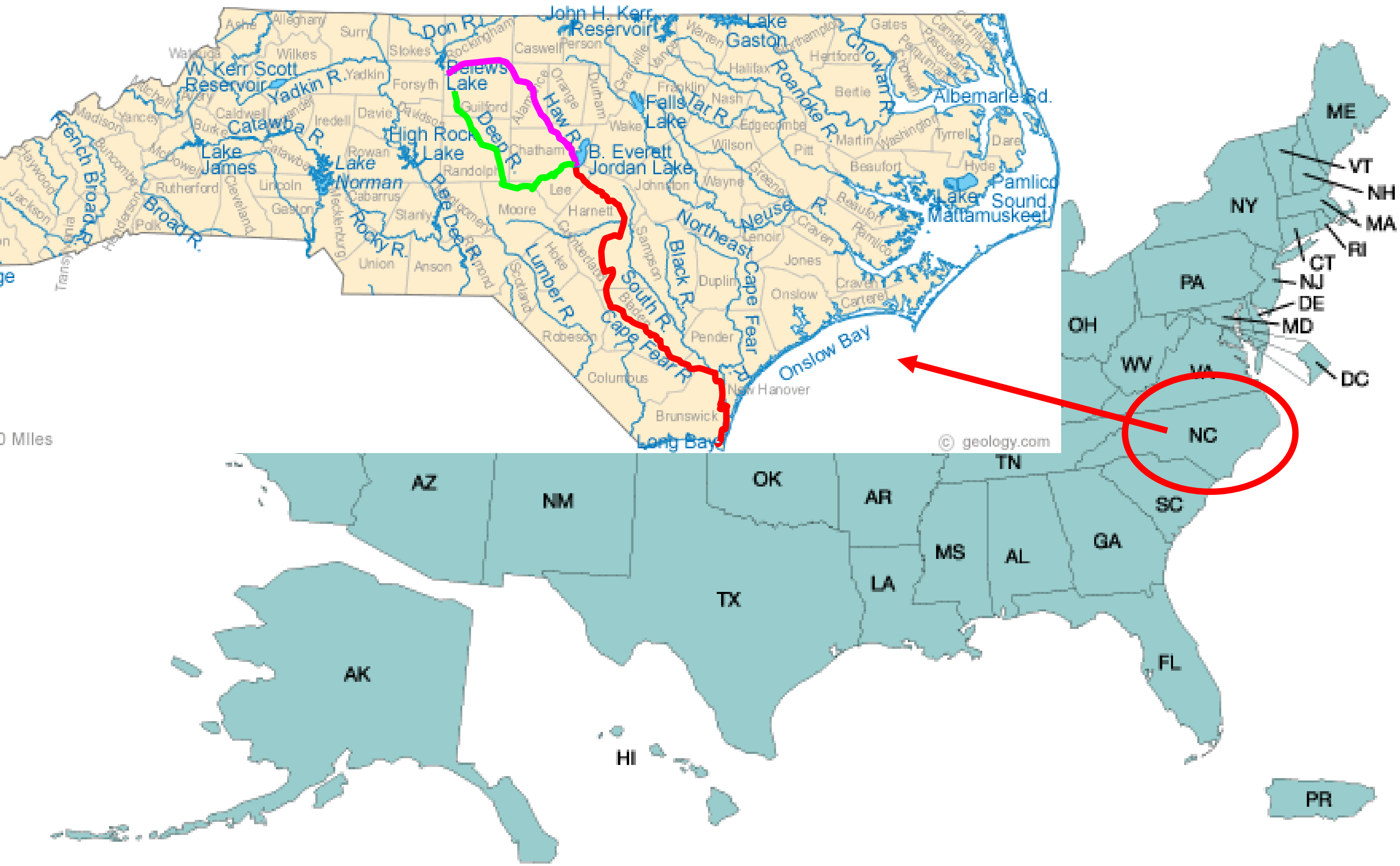
- Causes liver, immune system, developmental, endocrine, metabolic, and neurobehavioral toxicity.
- PFOA and PFOS caused tumors in chronic rat studies.

Human health effects associated with PFC(s) in the general population and/or communities with contaminated drinking water include:

- ↑ cholesterol
- ↑ uric acid
- ↑ liver enzymes
- ↓ birth weight
- ↓ vaccine response
- Thyroid disease
- Osteoarthritis
- Diabetes
- Testicular and kidney cancer
- Pregnancy-induced hypertension
- Ulcerative colitis
- Effects in young adulthood from prenatal exposures
  - *Obesity in young women.*
  - *↓ sperm count in young men.*



The Cape Fear River Basin

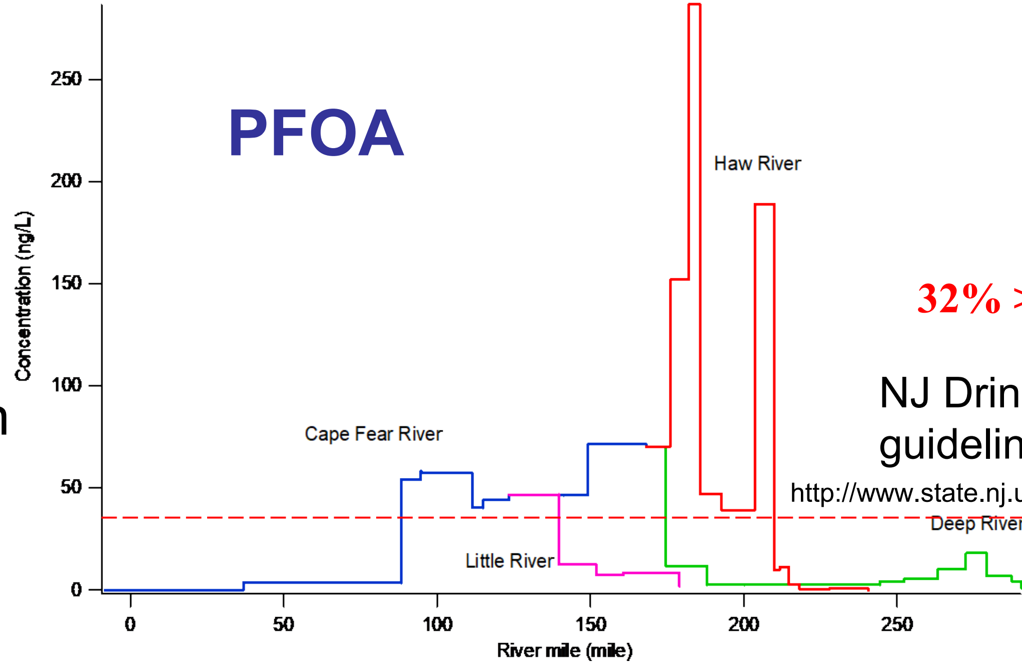


Survey of perfluorinated compounds in surface water 2006

SS Kemmerer sampler

Lab-made dip sampler

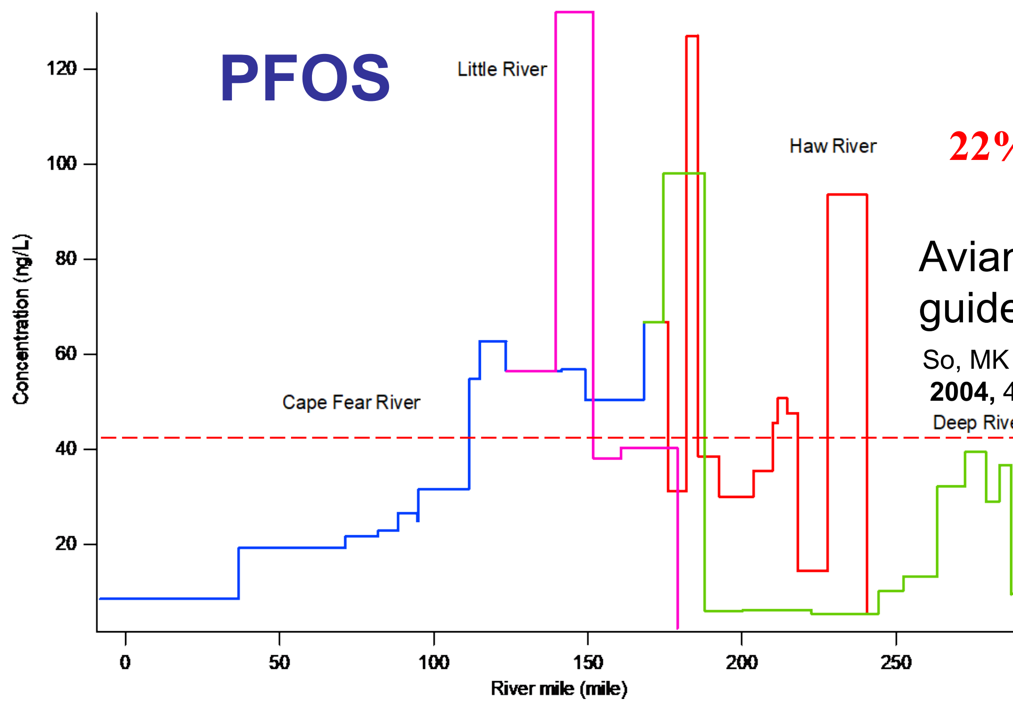
PFC profiles in the Cape Fear Drainage Basin, North Carolina, USA



32% > 40 ng/L

NJ Drinking water guideline 40 ng/L

http://www.state.nj.us/dep/watersupply/pfoa.htm



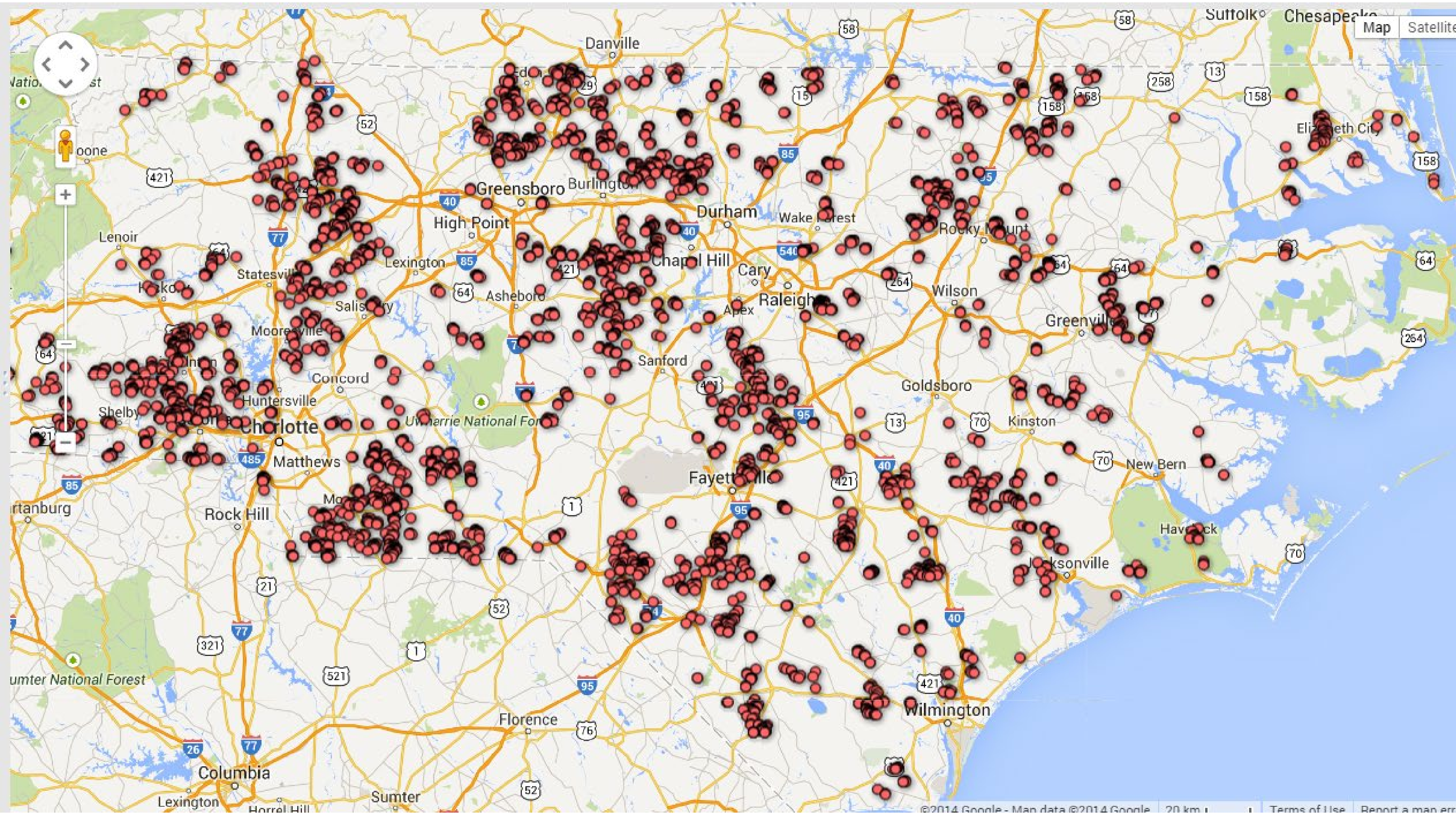
22% > 43 ng/L

Avian wildlife guideline 43 ng/L

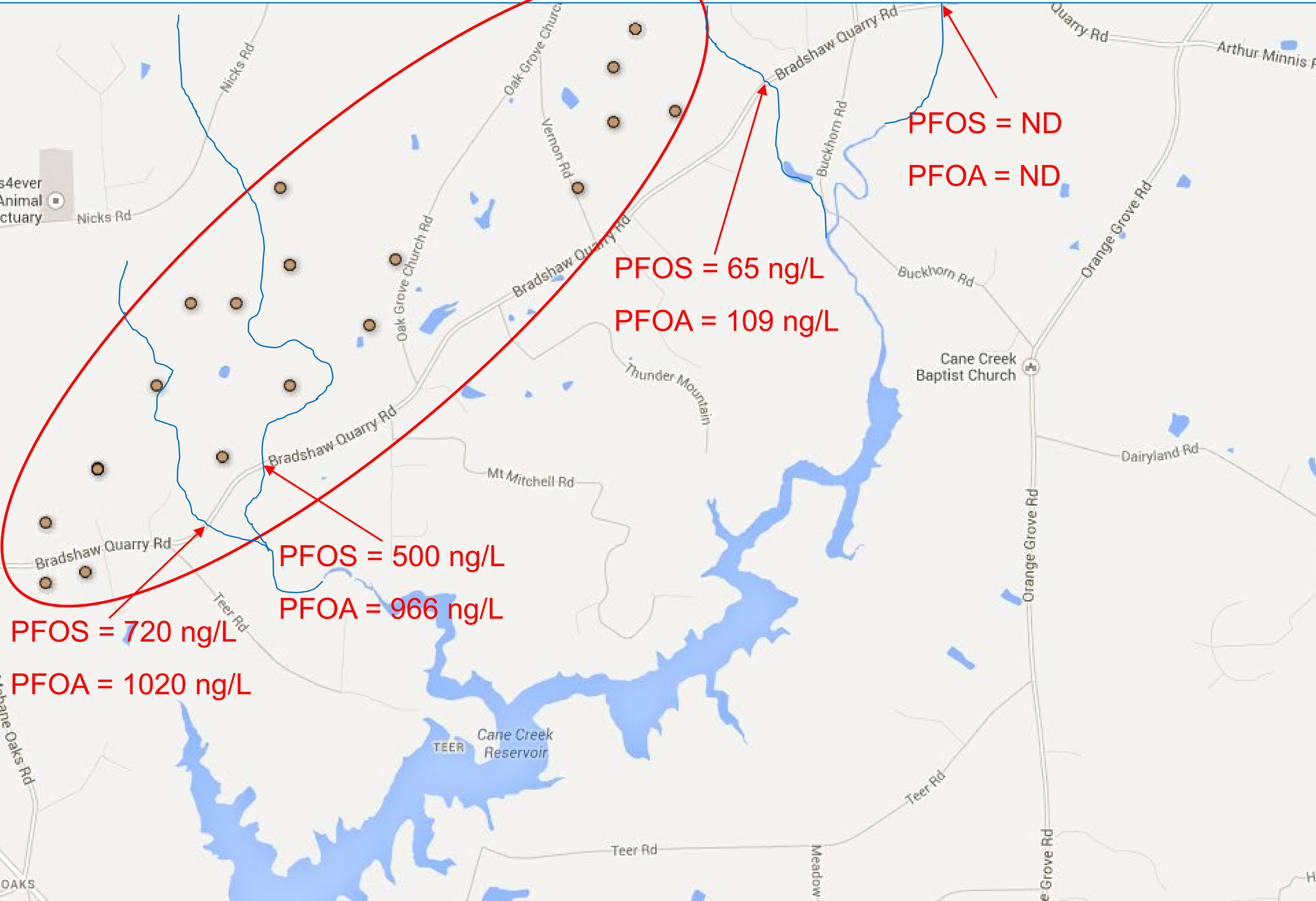
So, MK *et al. Environ. Sci. Technol.* **2004,** 4056-4063.

Nakayama *et al. Environ. Sci. Technol.* **2007,** 41: 5271-5276

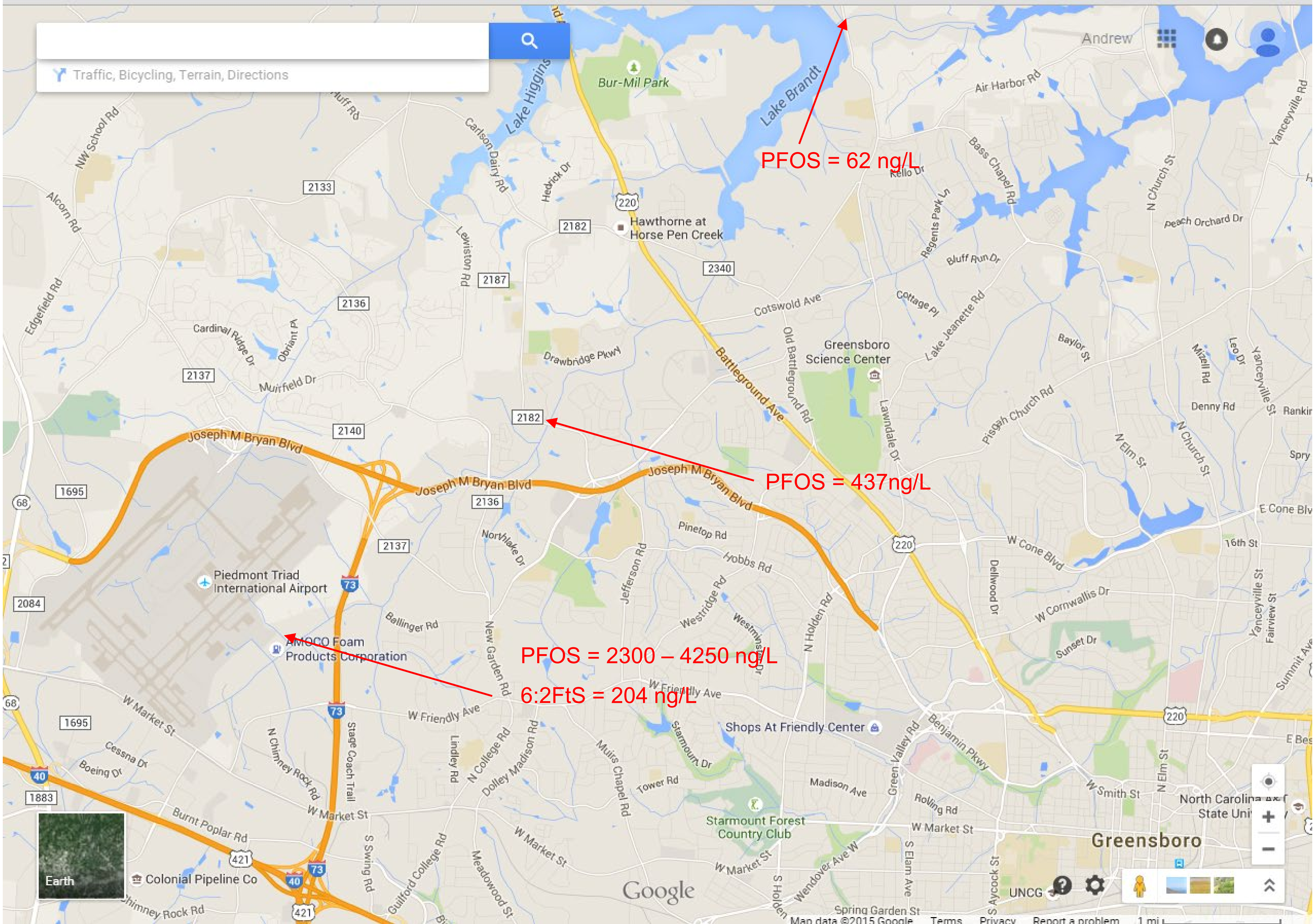
5,258 Permitted sludge application sites in North Carolina



Cane Creek Resevoir - Serving Orange County



PFOS in Surface water, Greensboro, North Carolina



US Environmental Protection Agency PFOA Stewardship Program

- In January 2006, USEPA started this program to help minimize impact of PFOA in the environment

- Eight major international companies have agreed to participate (including 3M, DuPont, Asahi Glass, Daikin)

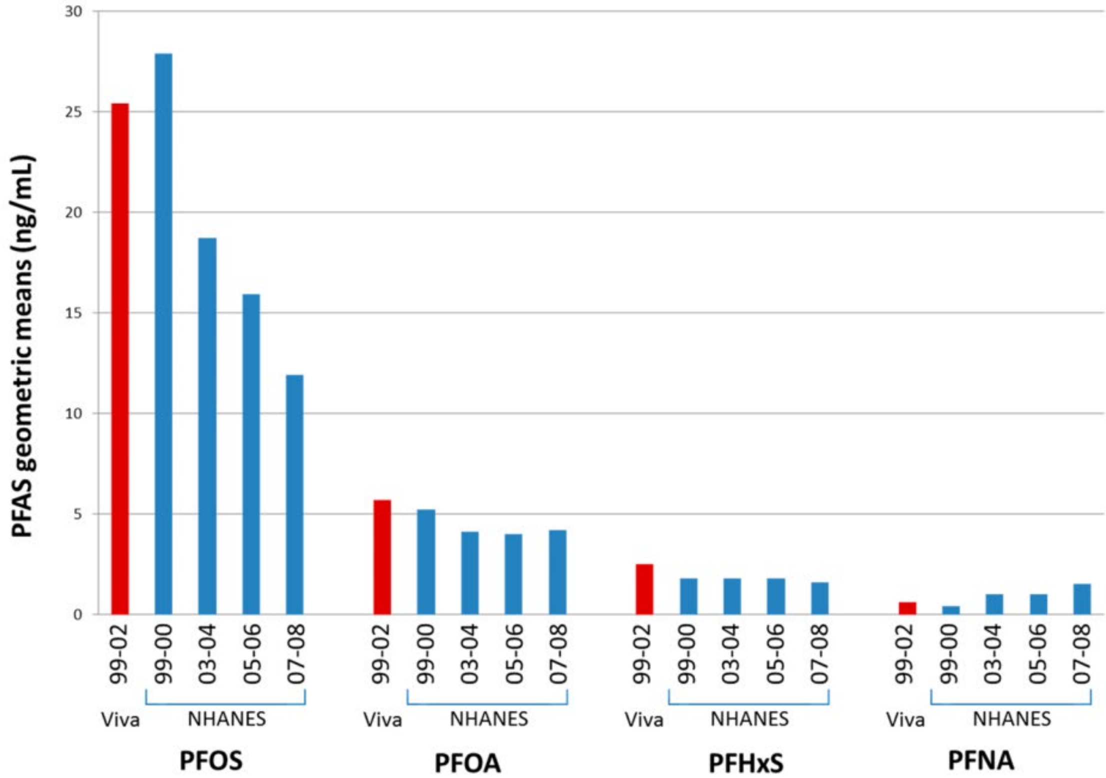
- Agreement to voluntarily reduce factory emissions and product content of PFOA and related compounds* on a global basis by 95% no later than 2010

- Agreement to work toward total elimination of emissions and product content of these compounds by 2015

- Based on emissions and content determinations made for 2006

* Includes PFOA, precursor chemicals that can break down to PFOA, higher homologues (C9 and larger)

Trends in PFAS Serum Levels in US



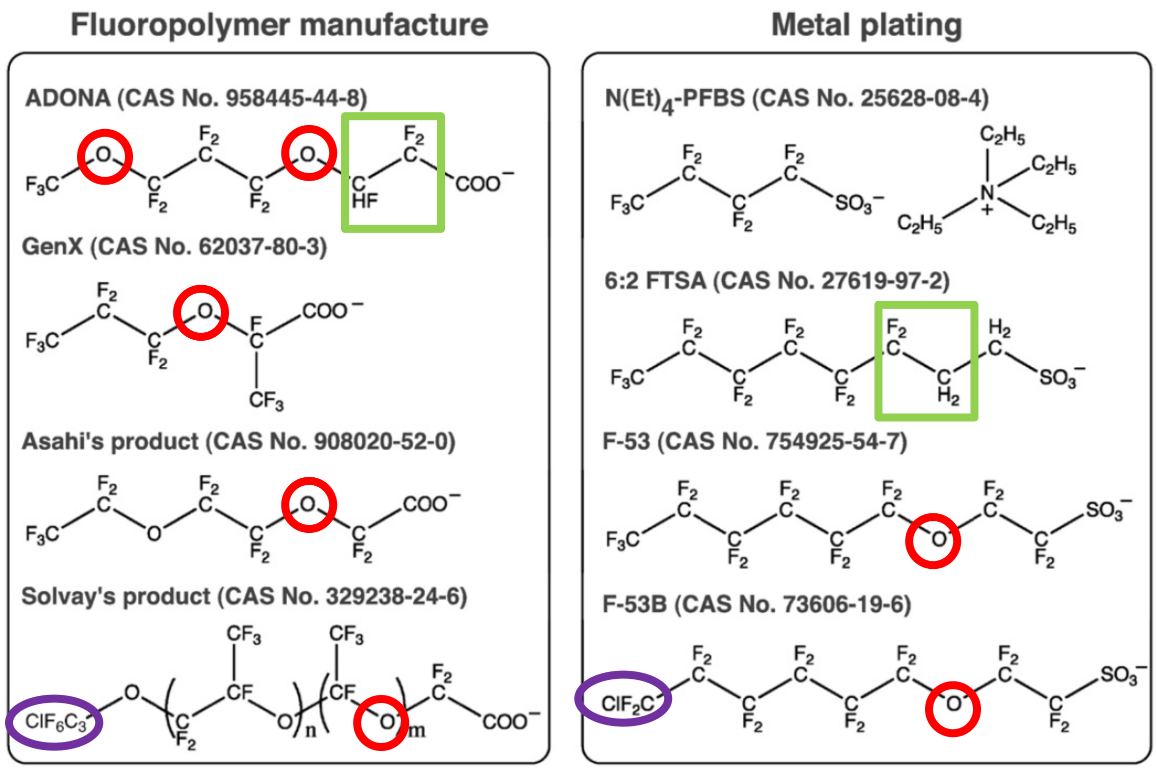
Sagiv et al. *Environmental Science & Technology* 2015, 49, 11849−11858

Table 2. Geometric mean and 95% confidence interval and selected percentiles of PFOS, PFOA, PFHxS, and PFNA serum concentrations (ng/mL) for the U.S. population 12 years of age and older: Data from NHANES 2011-2012 [a]

	Geometric Mean (95% Confidence Interval)		Selected Percentiles			
			50th	75th	90th	95th
PFHxS	1.28	1.15-1.43	1.27	2.26	3.81	5.43
PFOS	6.31	5.83-6.82	6.51	10.48	15.62	21.68
PFOA	2.08	1.95-2.22	2.08	3.02	4.35	5.67
PFNA	0.88	0.80-0.97	0.86	1.30	1.95	2.54

[a] CDC (2015)

PFAS Not Covered Under Stewardship Program



Wang et al. *Environment International*, **2013,** *60,* pp 242–248

Unknown Characteristics of “Emerging” Fluorinated Compounds

- Actual identities of alternatives unknown in industrial sectors and geographical regions that are not well regulated

- Data on environmental and human health effects are incomplete (at best) and more often nonexistent

- Data on degradability, bioaccumulation, and toxicity (environmental and human) are incomplete (at best) or completely lacking

- Information on production volume and environmental emissions not available

Wang et al. *Environment International* 2013, 60, 242−248

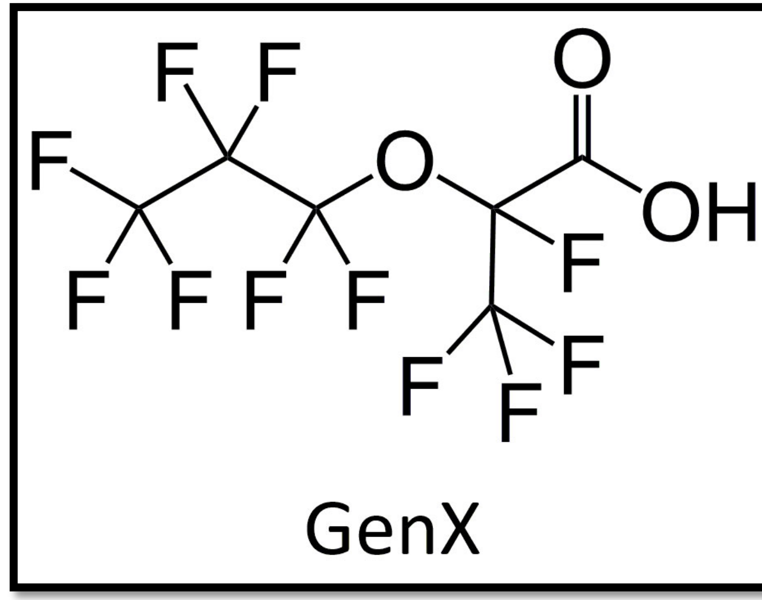
GenX

- Substitute for PFOA, identity originally protected as Confidential Business Information (CBI)

- Still persistent, still toxic, but less bioaccumulative than PFOA

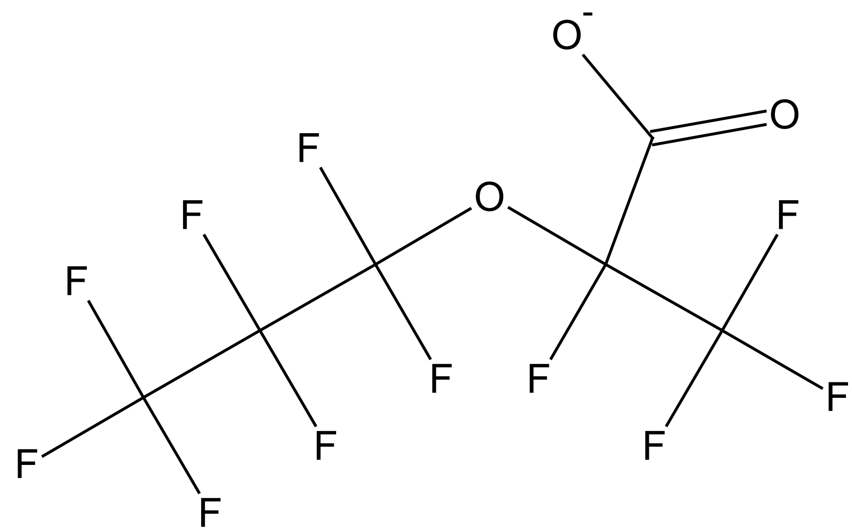
- DuPont studies found effects on rats similar to PFOA, including possible endocrine/immune disruption, enlarged livers and kidneys, and cancer

- Approved by the EPA, used for production of Teflon



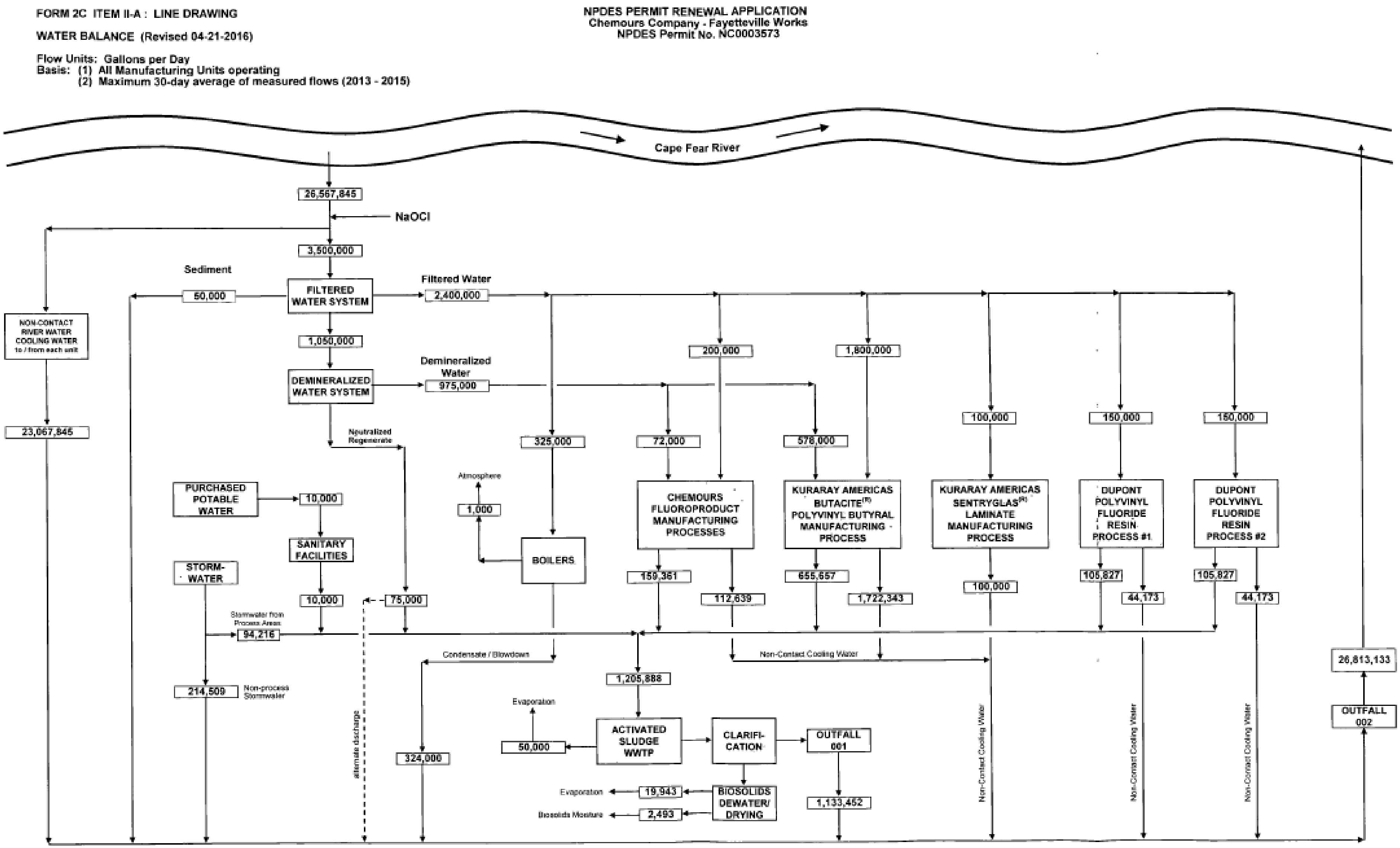
GenX: (2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid)

- Class: PFECAs
- Formula: $C_6HF_{11}O_3$
- CAS no.: 13252-13-6
- Molecular Mass: 329.9750 Da
- Ref: Strynar et al., ES&T 2015;
Sun et al., 2016

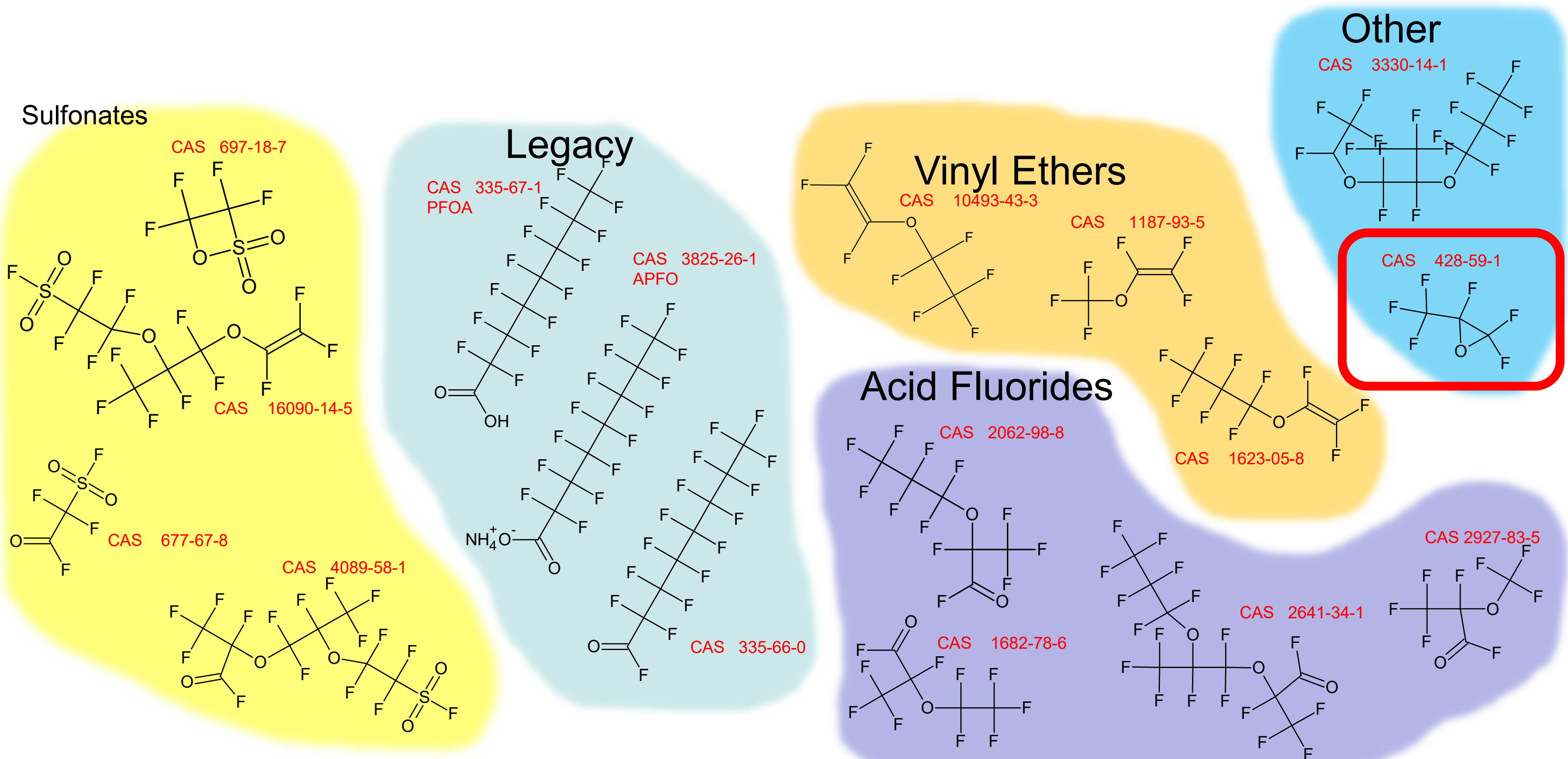


Chemours Fayetteville Works Plant, Bladen County, NC

Permit Process Schematic

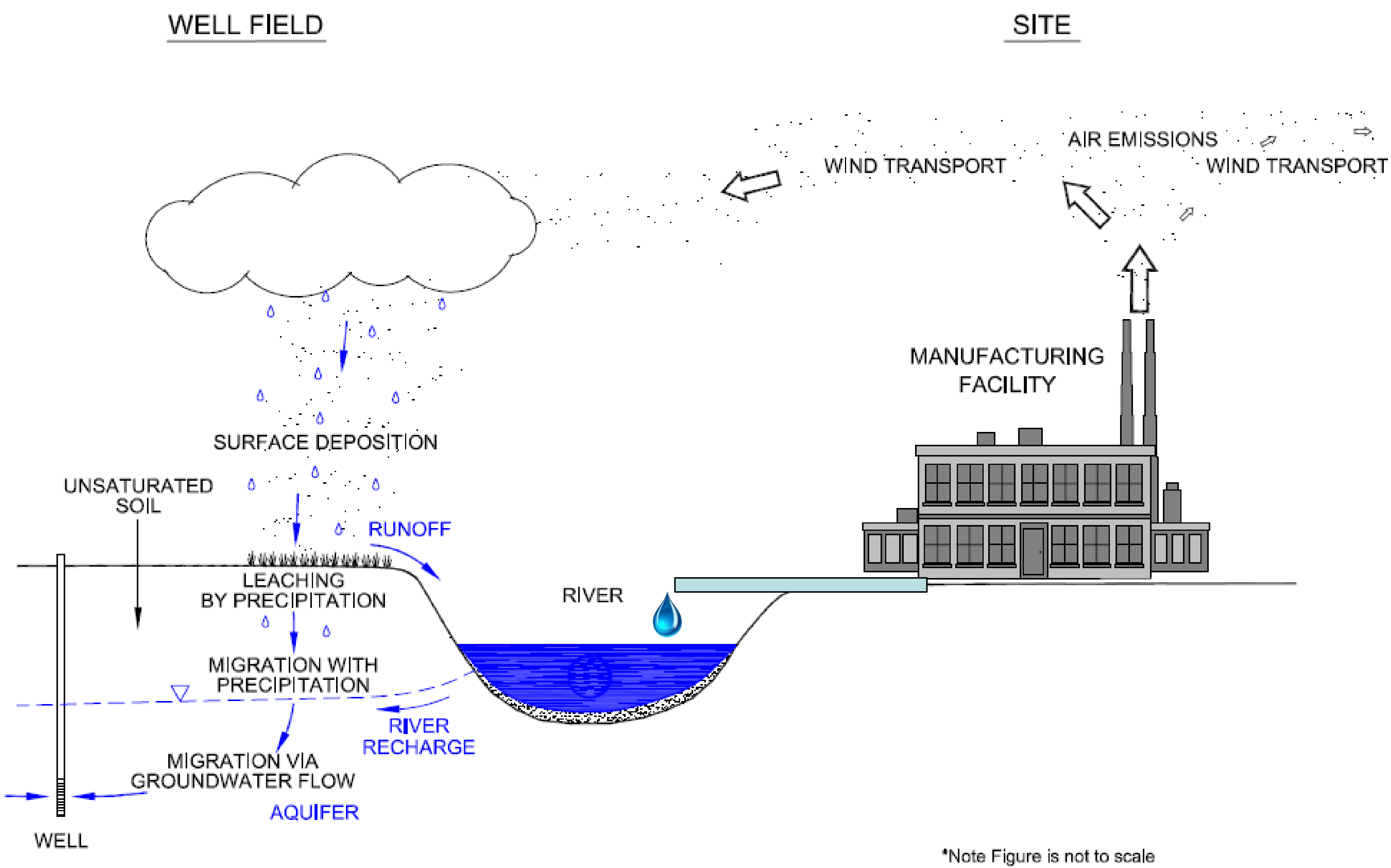


Chemours Site TSCA Inventory

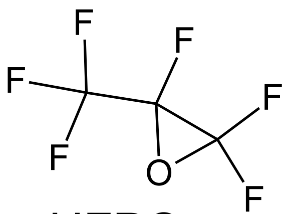


DUPONT FAYETTEVILLE PLANT
22828 NC HIGHWAY 87 WEST
FAYETTEVILLE, NC 28306-7332

http://iaspub.epa.gov/enviro/tsca.get_chem_info?v_registry_id=110000559609



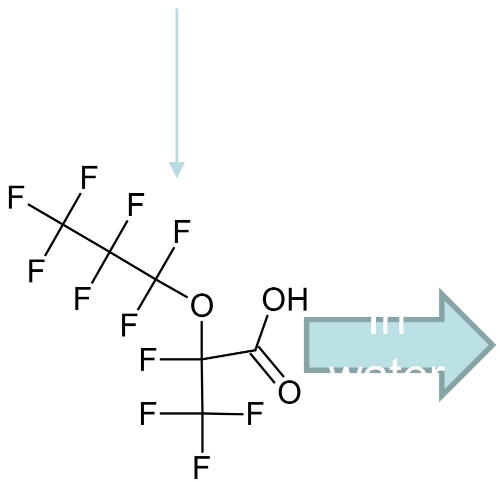
Davis et al. Chemosphere 67 (2007) 2011–2019



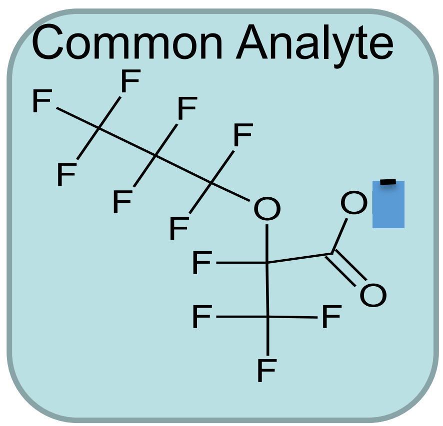
HFPO
CAS 428-59-1

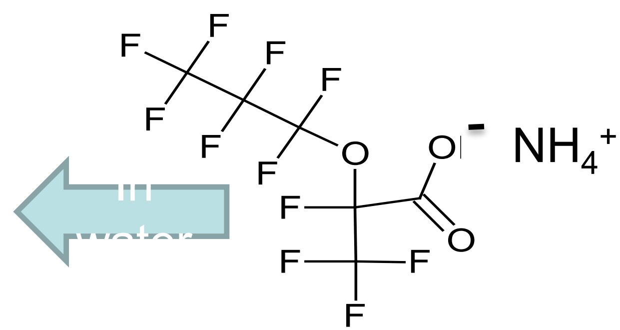
Hexafluoropropylene oxide (HFPO)

- an intermediate used in industrial organofluorine chemistry
- a monomer for fluoropolymers.
- colorless gas is
  the epoxide of hexafluoropropylene
- produced by DuPont and 3M and as a precursor to the lubricant Krytox and related materials
- generated by oxidation of perfluoropropylene, e.g. with oxygen as well as other oxidants



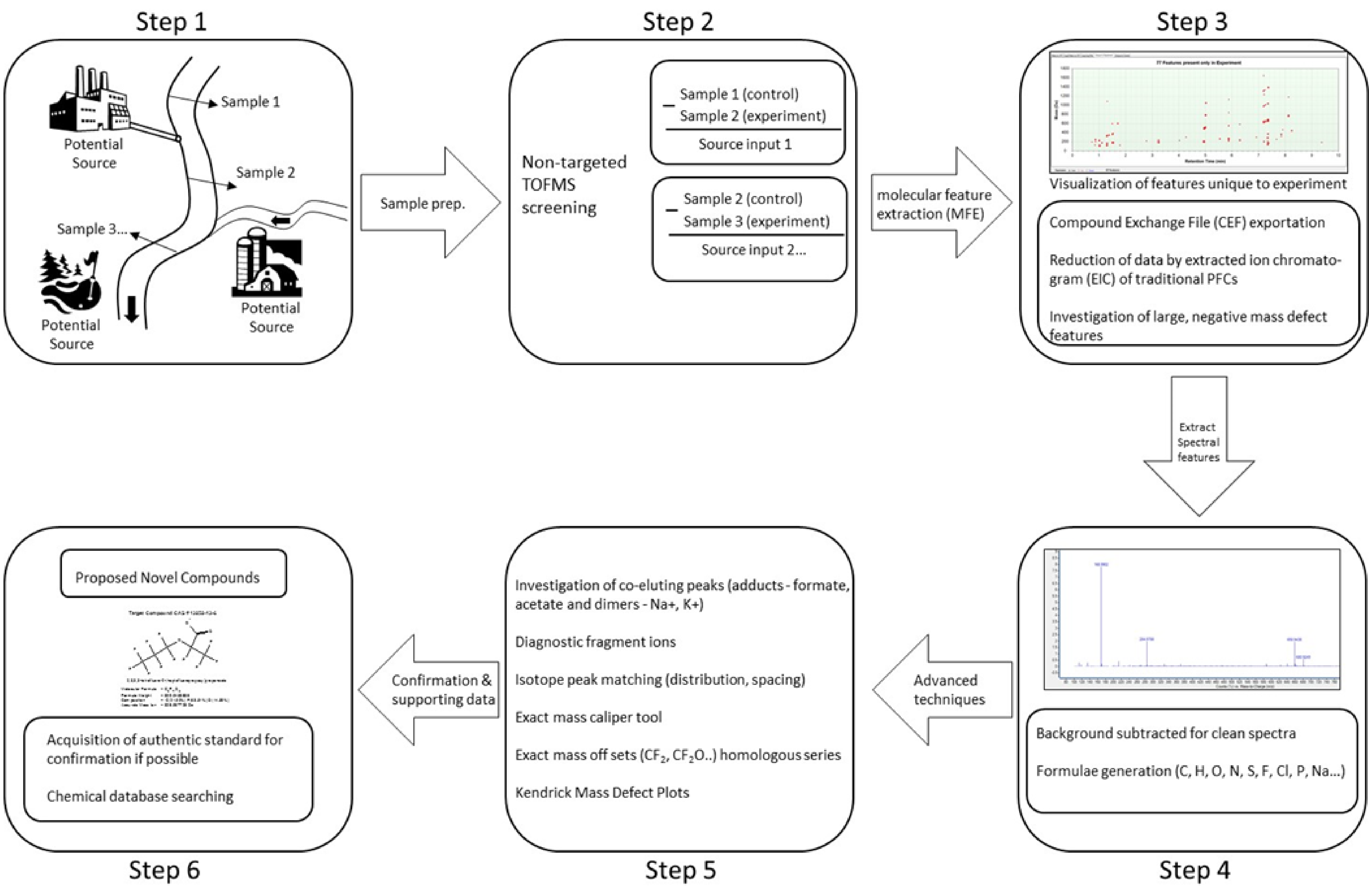
HFPO DA
CAS 13252-13-6





GenX
CAS 62037-80-3

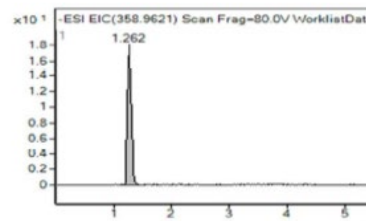
High Resolution Mass Spectrometry Non Targeted Analysis (NTA)



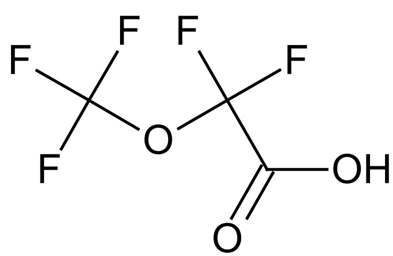
Strynar et al. *Environmental Science & Technology* 2015, 49, 11622−11630

Non-Targeted Methods

- High resolution mass spectrometry allows one to observe an unknown compound as a peak in a chromatogram and to ultimately predict the identity of this unknown
- Initially, the mass spectrometer assigns a mass for each peak observed, for example 179.9846 Daltons (Da)



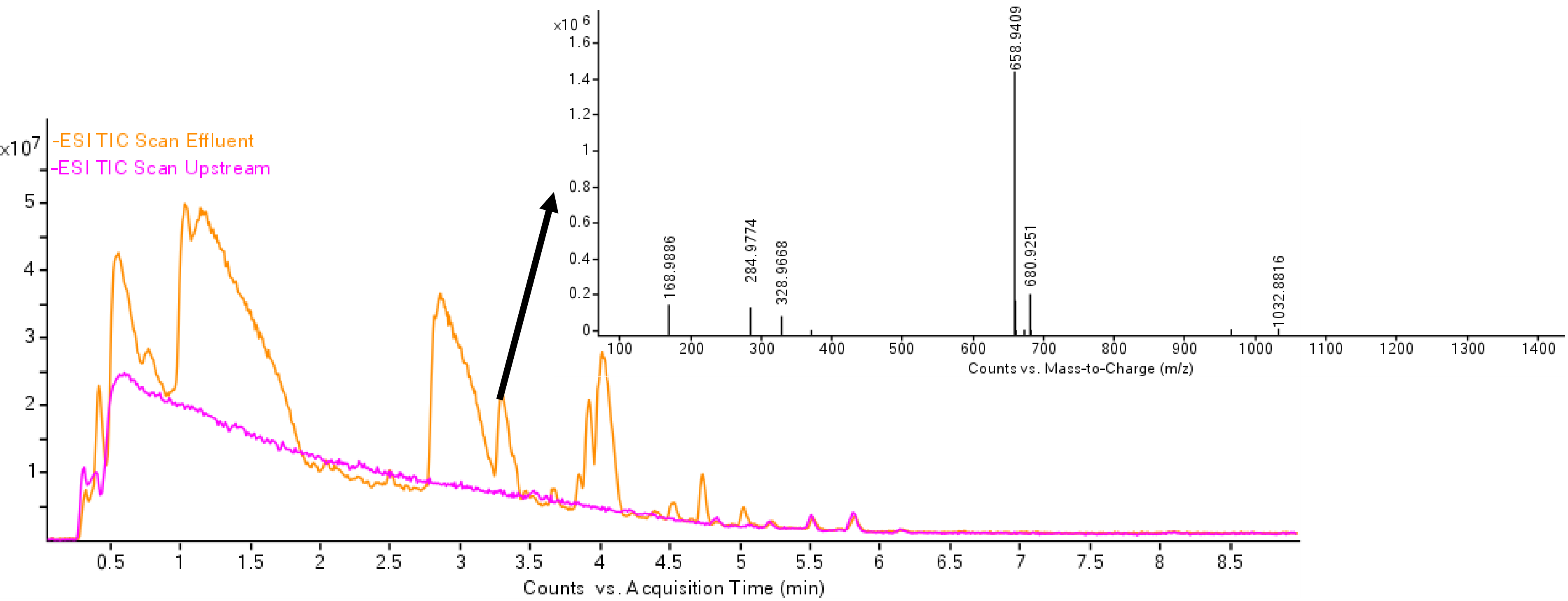
- Software then calculates the exact number and type of atoms needed to achieve that measured mass, example $C_3HF_5O_3$ (need this number and type of atoms to weigh this much)
- Software and fragmentation experiments allow determination of most likely structure:



Molecular Formula: $C_3HF_5O_3$
Monoisotopic Mass: 179.984585 Da
[M-H]-: 178.977308 Da

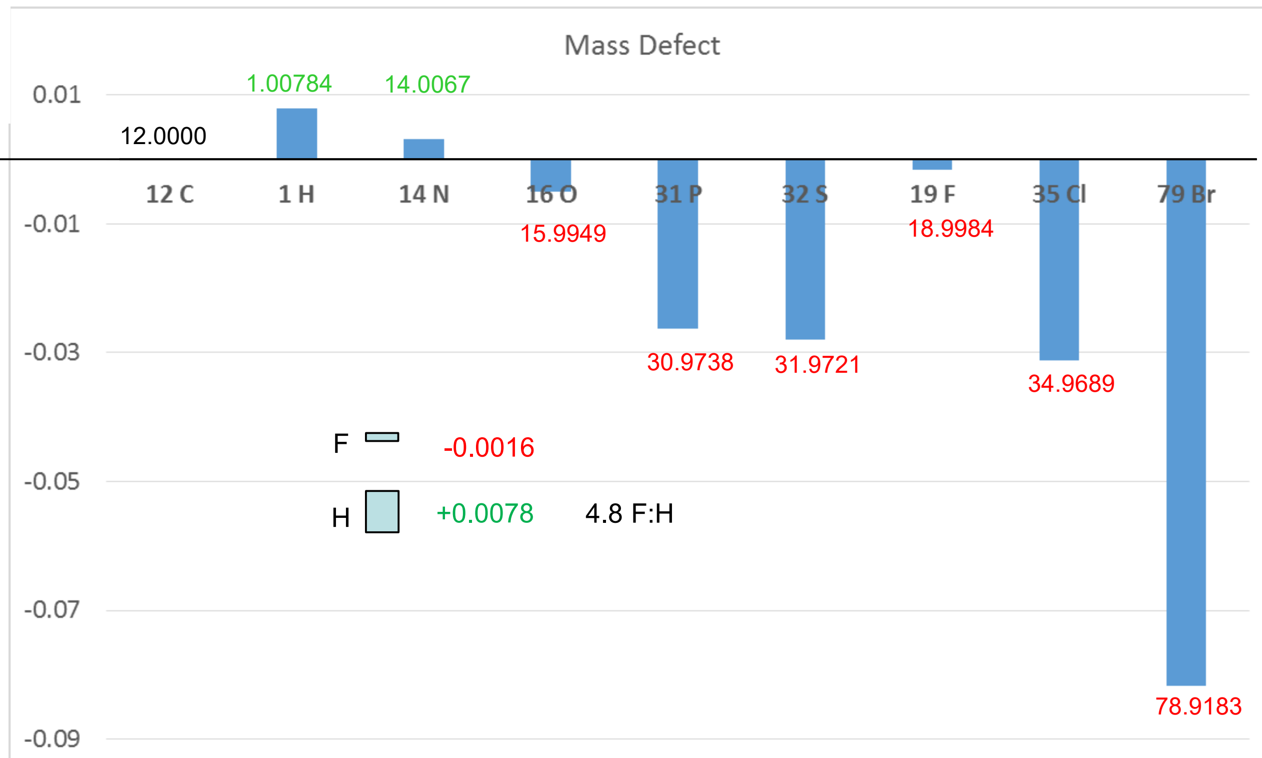
- With mass, formula, and structure determined, identity can be assigned by searching against databases of known compounds, example CAS number 674-13-5
- Search for standards from commercial sources to confirm identification if possible

Chromatographic and High Resolution Mass Spectrophotometric Data



Isotope Signatures: Negative Mass Defect

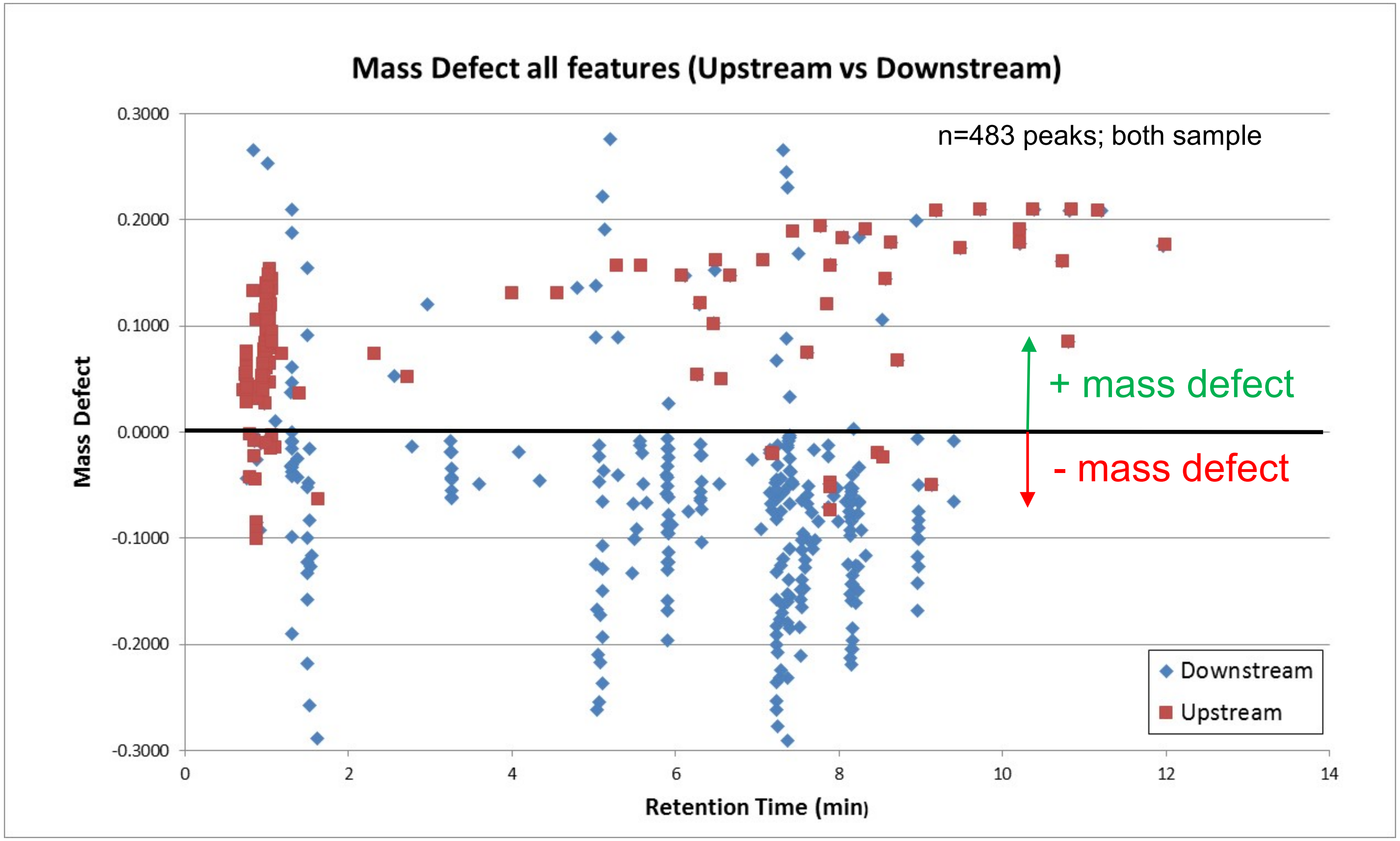
Positive Mass Defect



Negative Mass Defect

Mass Defect Plot TOFMS data

Accurate Mass – Nominal Mass = Mass Defect



Environmental Science & Technology

Article

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Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

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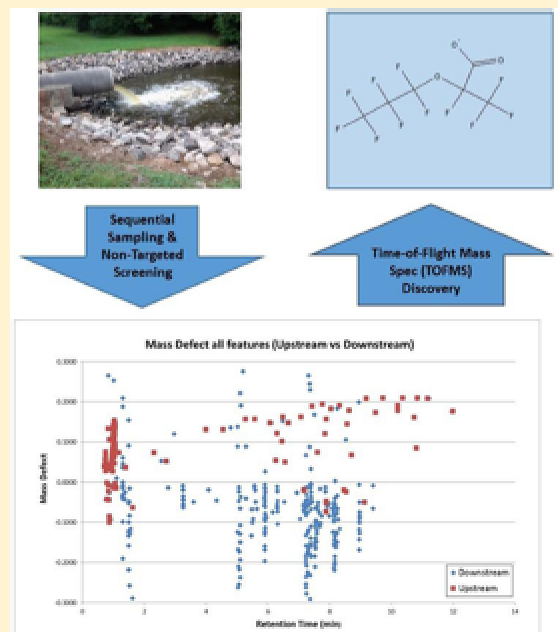
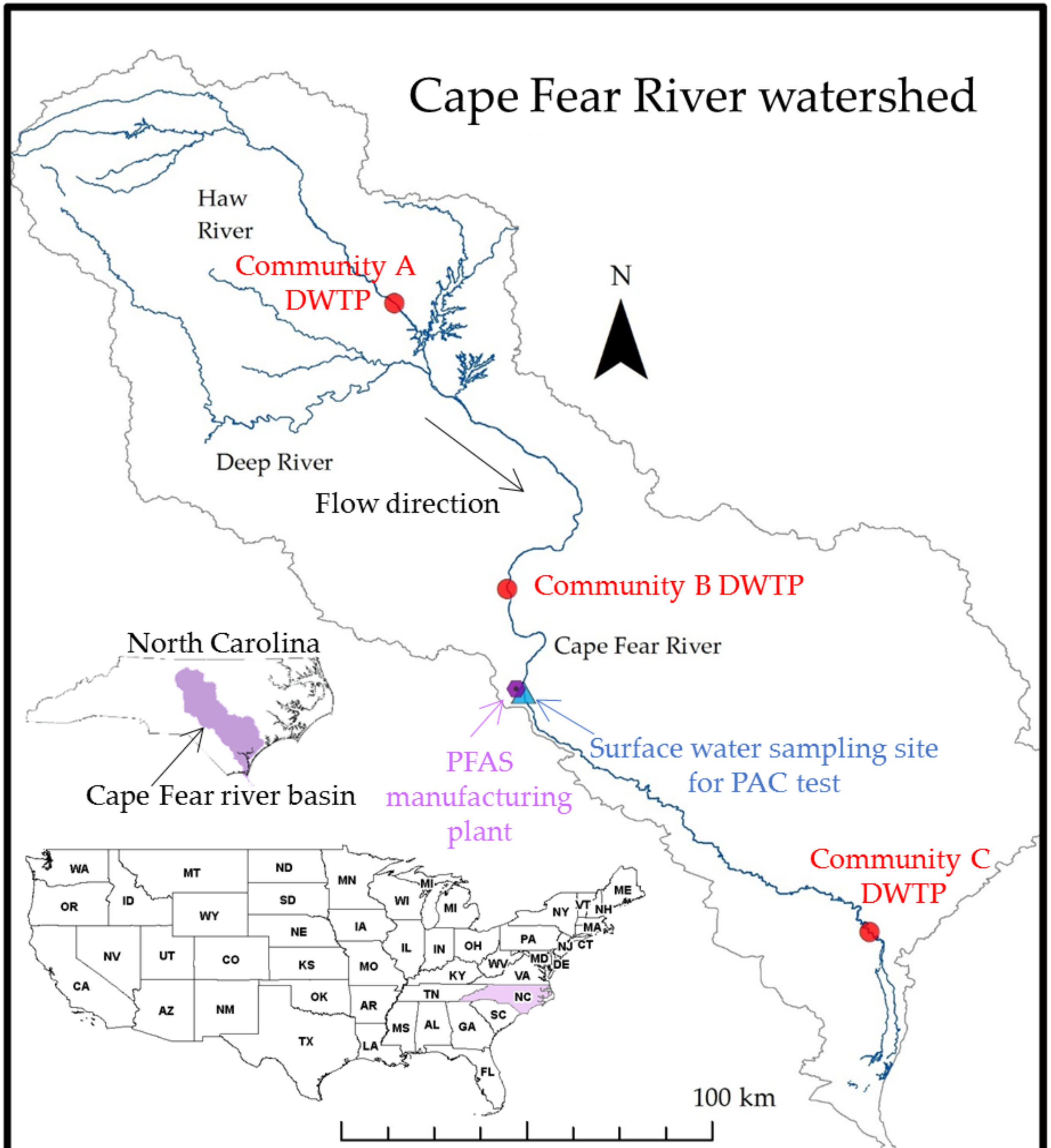
[⊥]Agilent Technologies Inc., Wilmington, Delaware 19808, United States

Supporting Information

ABSTRACT: Recent scientific scrutiny and concerns over exposure, toxicity, and risk have led to international regulatory efforts resulting in the reduction or elimination of certain perfluorinated compounds from various products and waste streams. Some manufacturers have started producing shorter chain per- and polyfluorinated compounds to try to reduce the potential for bioaccumulation in humans and wildlife. Some of these new compounds contain central ether oxygens or other minor modifications of traditional perfluorinated structures. At present, there has been very limited information published on these "replacement chemistries" in the peer-reviewed literature. In this study we used a time-of-flight mass spectrometry detector (LC-ESI-TOFMS) to identify fluorinated compounds in natural waters collected from locations with historical perfluorinated compound contamination. Our workflow for discovery of chemicals included sequential sampling of surface water for identification of potential sources, nontargeted TOFMS analysis, molecular feature extraction (MFE) of samples, and evaluation of features unique to the sample with source inputs. Specifically, compounds were tentatively identified by (1) accurate mass determination of parent and/or related adducts and fragments from in-source collision-induced dissociation (CID), (2) in-depth evaluation of in-source adducts formed during analysis, and (3) confirmation with authentic standards when available. We observed groups of compounds in homologous series that differed by multiples of CF_2 (*m/z* 49.9968) or CF_2O (*m/z* 65.9917). Compounds in each series were chromatographically





Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415−419

November 2016

Environmental Science & Technology LETTERS

Letter

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Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

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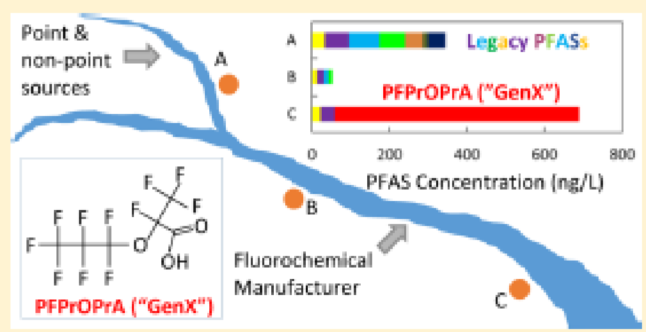
Supporting Information

ABSTRACT: Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctane-



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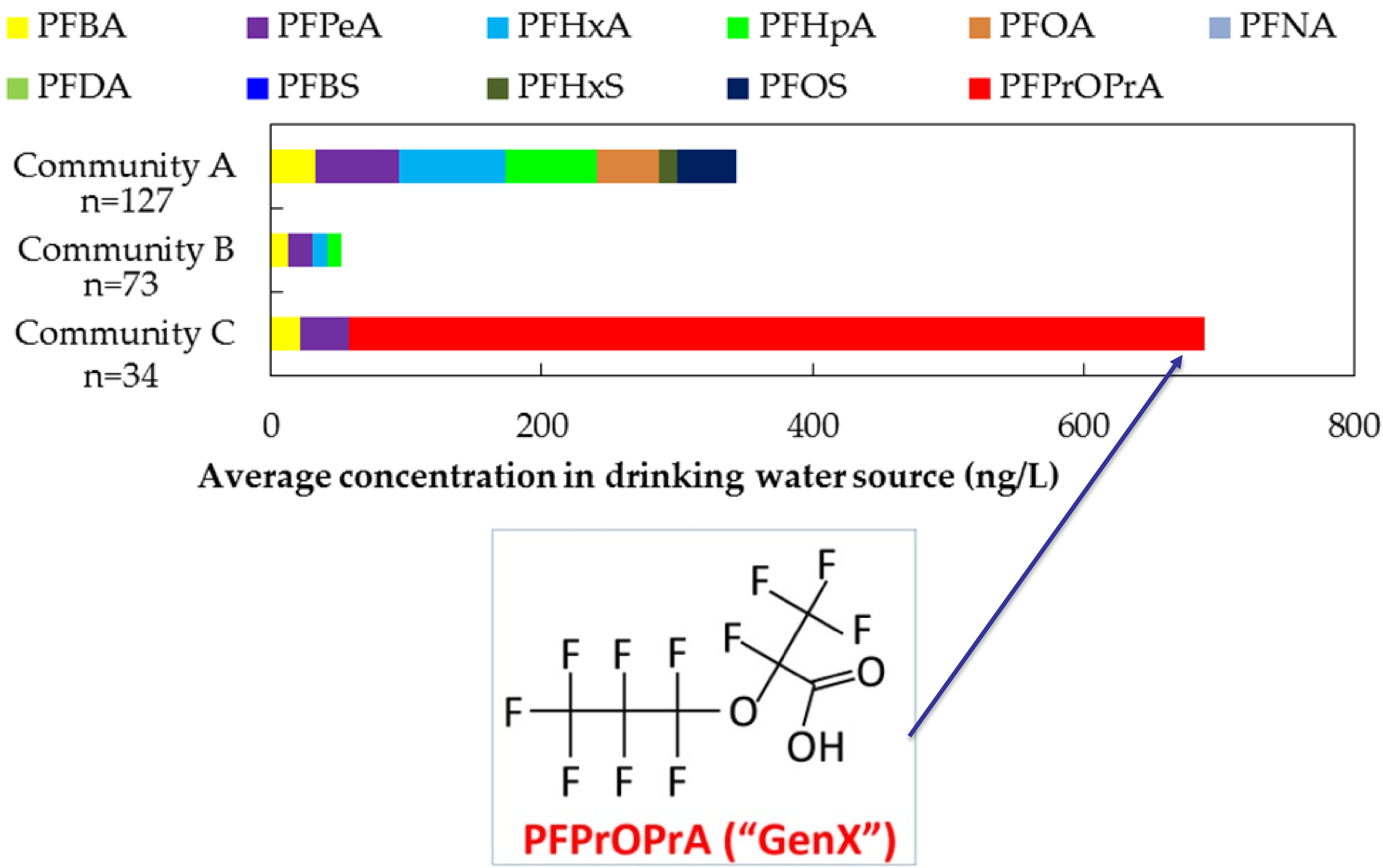
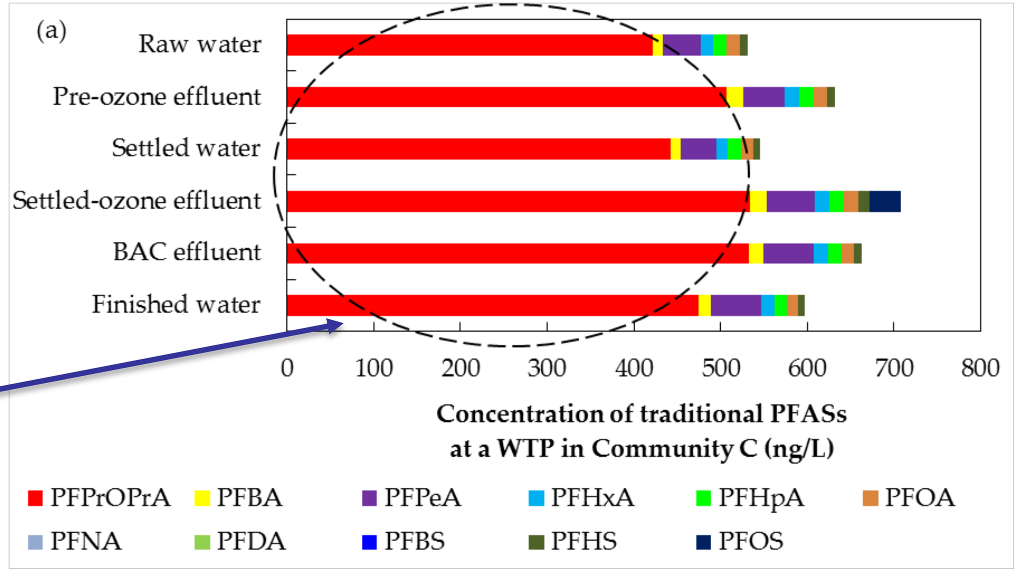
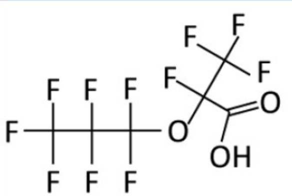
Legacy PFAS with GenX in Cape Fear River Basin



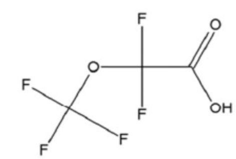
Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415−419

Emerging PFAS in Wilmington Drinking Water

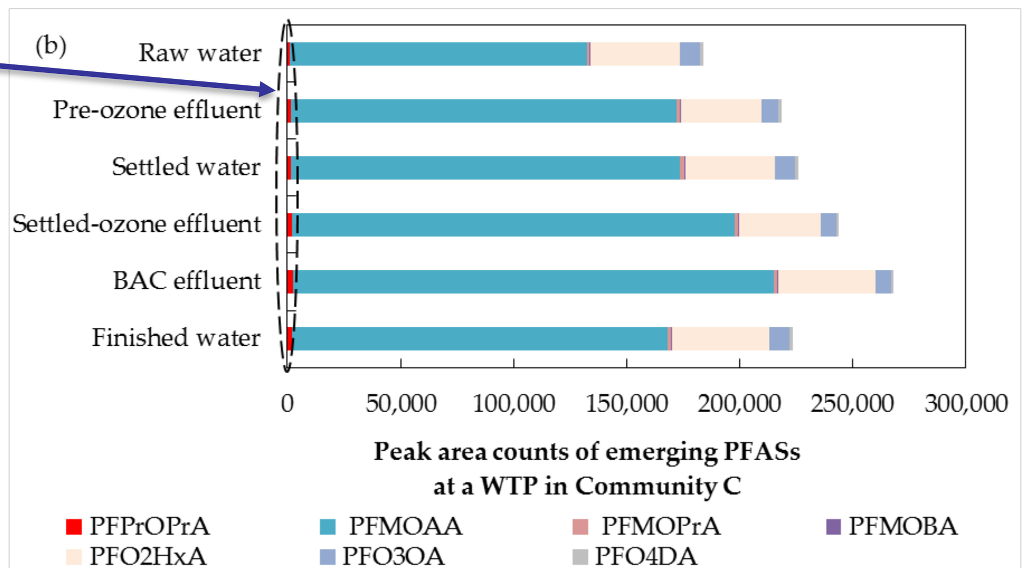


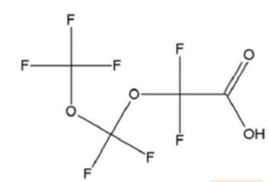


PFPrOPrA ("GenX")

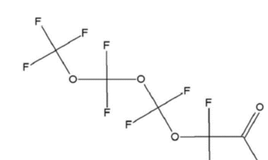


PFMOAA



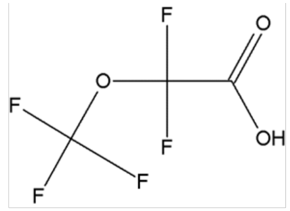


PFO2HxA



PFO3OA

Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415−419



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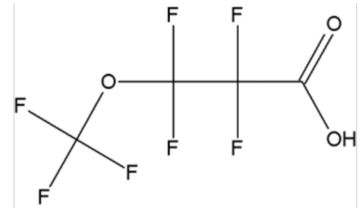
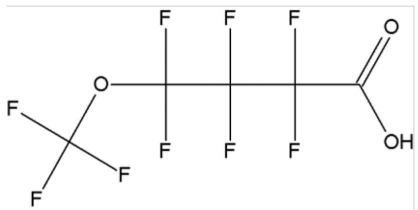


PFMOPrA



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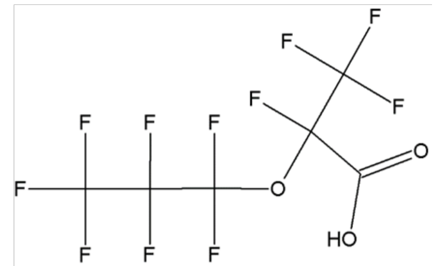

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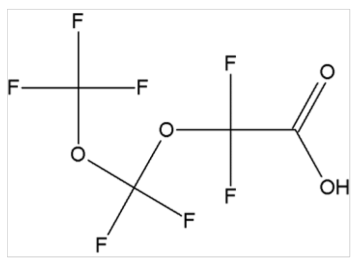
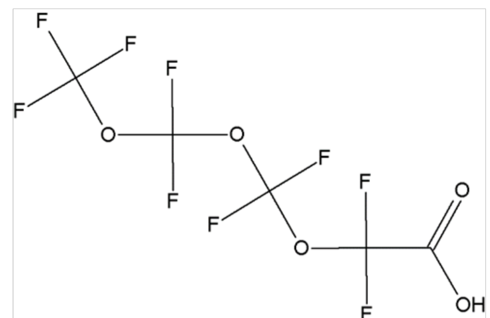
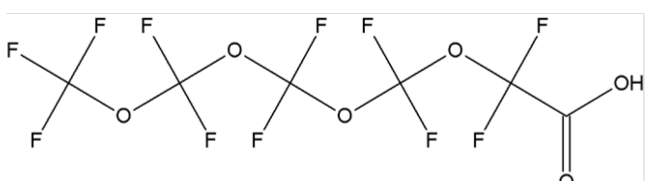


PFO2HxA



PFO3OA



PFO4DA

Sun et al. *Environmental Science & Technology Letters* 2016, 3, 415−419

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StarNews 150th 1867 • 2017

Toxin taints CFPUA drinking water

MOST POPULAR

1 Carolina Surf condos - in danger of collapse - condemned, evacuated
Jul 2 at 5:50 AM

2 Man injured by hook, not bit by shark at Wrightsville Beach
Jun 30 at 1:43 PM

3 Murder suspect had other charges pending
Jul 2 at 5:44 AM

4 Residents not allowed back into Carolina Surf condos
Jul 4 at 7:33 AM

OUR PICKS

HIDE CAPTION

A 2000 aerial photo of Fayetteville Works on the Cumberland-Bladen county line. The site, home to several plants, one of which makes GenX, is about 100 miles upstream from Wilmington. [COURTESY OF THE FAYETTEVILLE OBSERVER]

By Vaughn Hagerty StarNews Correspondent
Posted Jun 7, 2017 at 10:31 AM
Updated Jun 8, 2017 at 10:38 AM

Utility can't filter out chemical produced upriver

June 7, 2017 story on in Wilmington Star Online News

GenX contamination discovered and stopped

- Non-targeted analysis reveals previously unknown PFAS drinking water contamination

Environmental Science & Technology (Sept 2015) Article pubs.acs.org/est

Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

Mark Strynar,*,† Sonia Dagnino,†,‡ Rebecca McMahen,†,‡ Shuang Liang,†,‡ Andrew Lindstrom,† Erik Andersen,† Larry McMillan,§ Michael Thurman,∥ Imma Ferrer,∥ and Carol Ball⊥

- GenX quantified in drinking water

Environmental Science & Technology Letters (Nov 2016) Letter pubs.acs.org/journal/estlcu

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- Local news media picks up research reports

The Intercept_

NEW TEFLON TOXIN FOUND IN NORTH CAROLINA DRINKING WATER

Sharon Lerner

June 17 2017, 8:16 a.m.

(Jun 2017)

The Teflon Toxin Part 12

In this series, Sharon Lerner exposes DuPont's multi-decade cover-up of the severe harms to health associated with a chemical known as PFOA, or C8, and associated compounds such as PFOS and GenX.

- Chemours mitigates GenX discharge to Cape Fear River

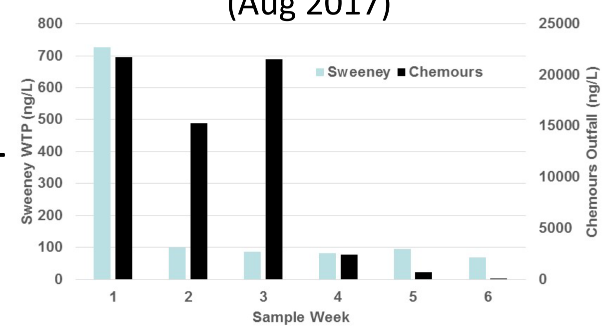
CHEMOURS SAYS IT WILL TAKE ADDITIONAL STEPS TO KEEP GENX FROM CAPE FEAR RIVER AS EPA, STATE BEGIN INVESTIGATIONS (Jun 2017)

By: WWAY News Submitted: 06/20/2017 - 10:41pm Buy This Video

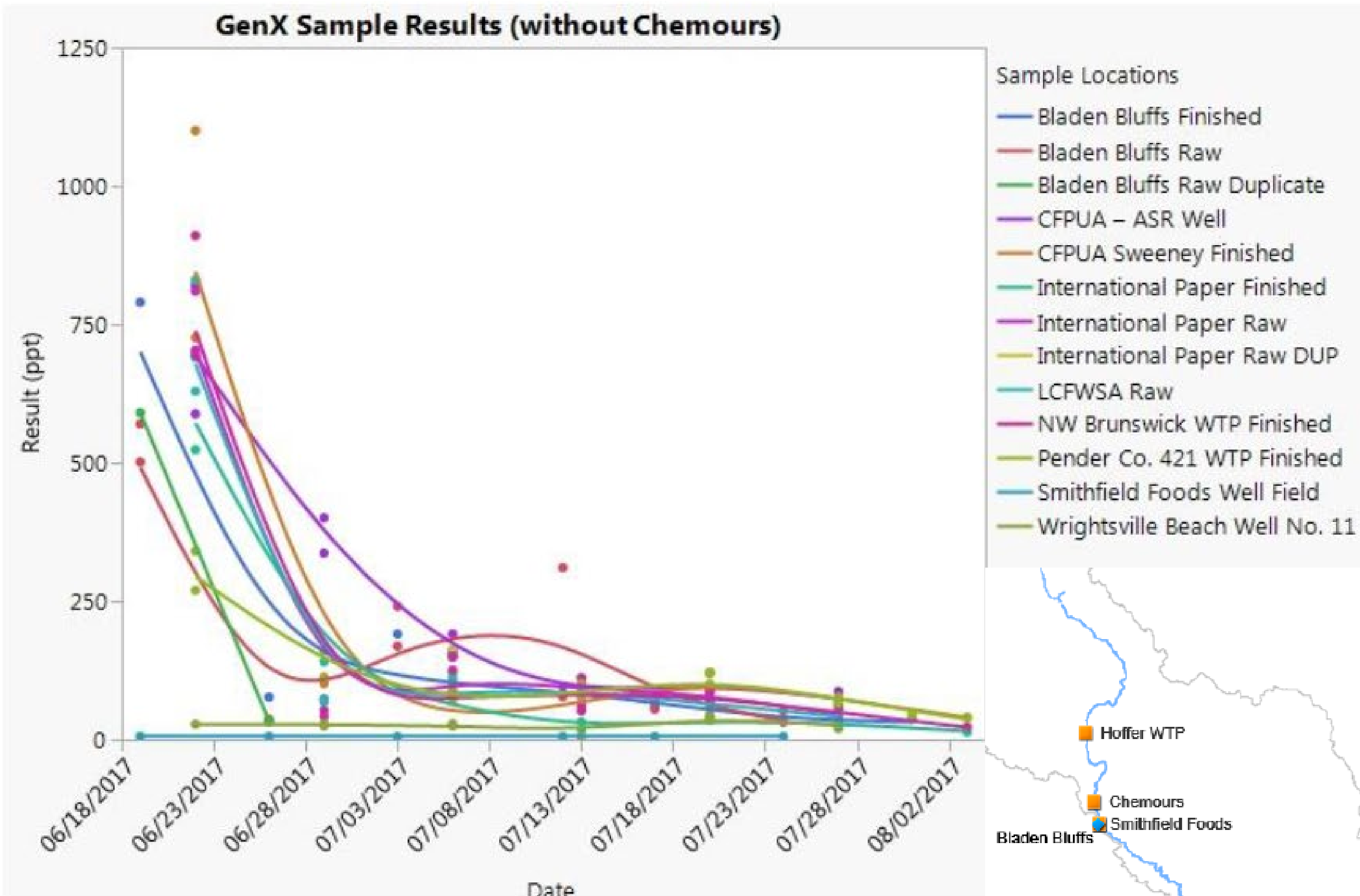
Tags: Cape Fear River, CFPUA, Chemours, Consumer, GenX, Health, Michael Regan, NC Department of Environmental Quality, NC Department of Health and Human Services, Water

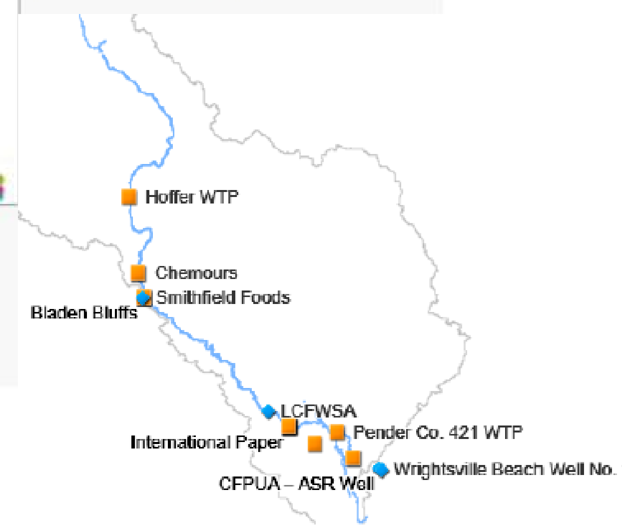
- NC DEQ, EPA (including Region 4 and ORD) partner to monitor mitigation effectiveness

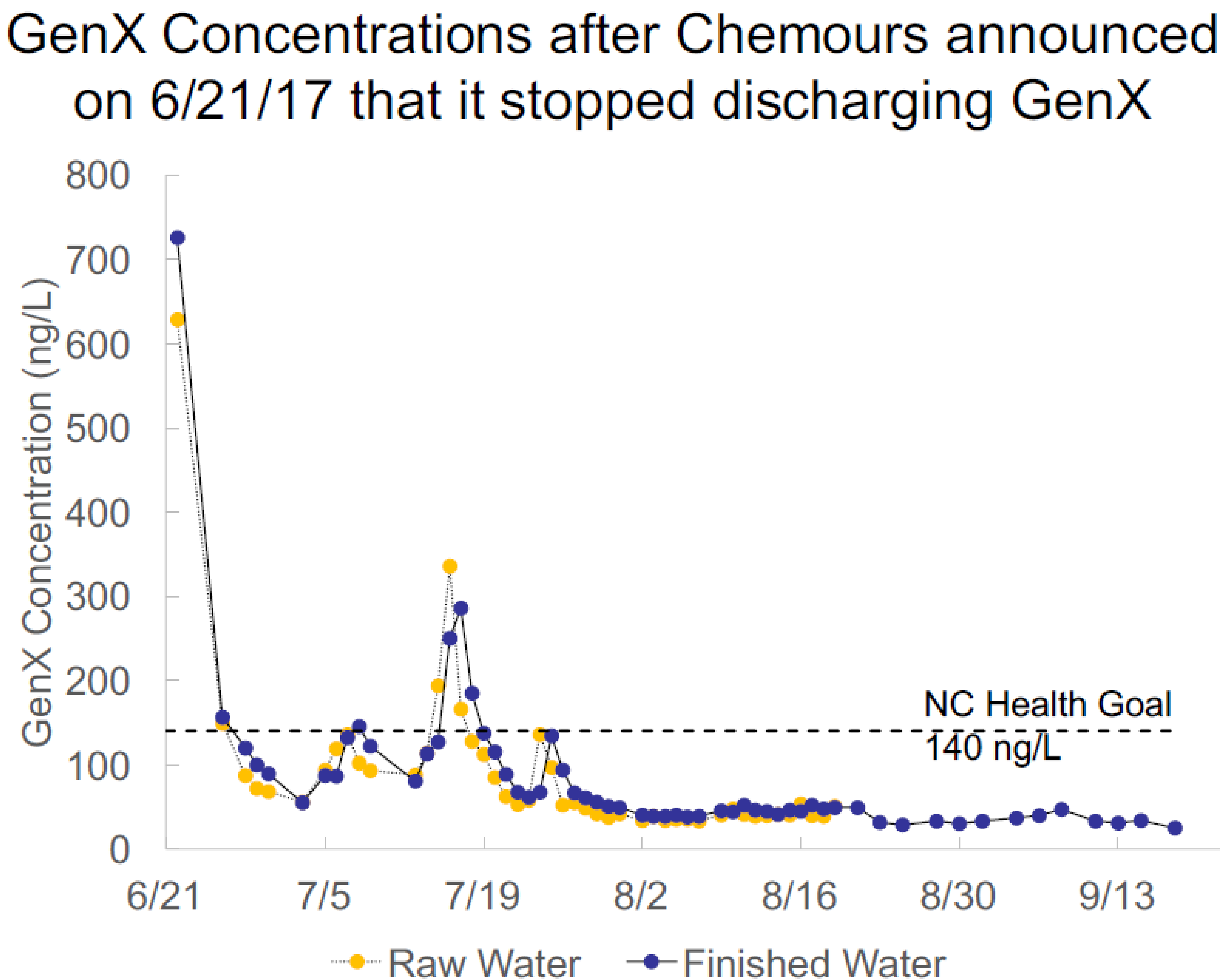
(Aug 2017)



GenX Reduction in Cape Fear River Basin 2017

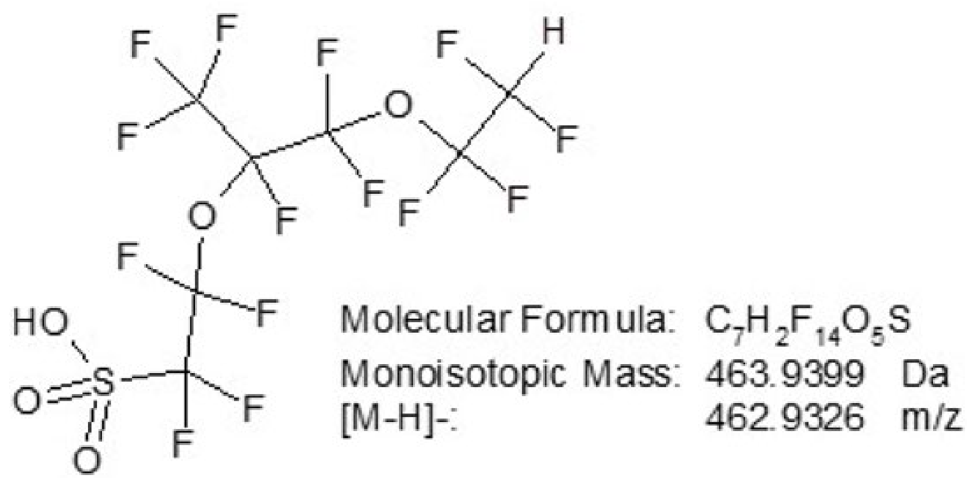




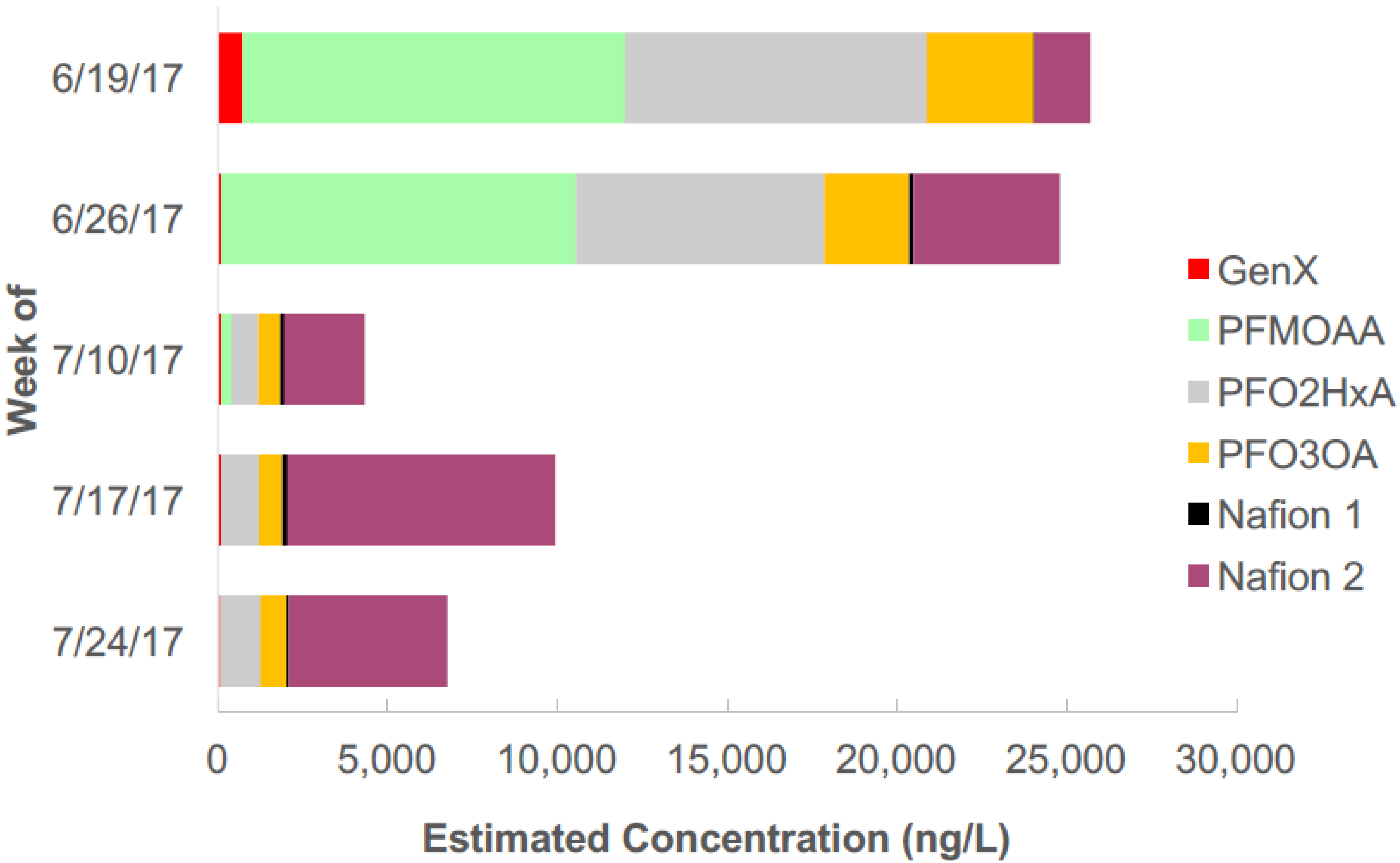

GenX Concentrations after Chemours announced on 6/21/17 that it stopped discharging GenX
GenX Concentration (ng/L)
800
700
600
500
400
300
200
100
0
6/21
7/5
7/19
8/2
8/16
8/30
9/13
NC Health Goal
140 ng/L
Raw Water
Finished Water

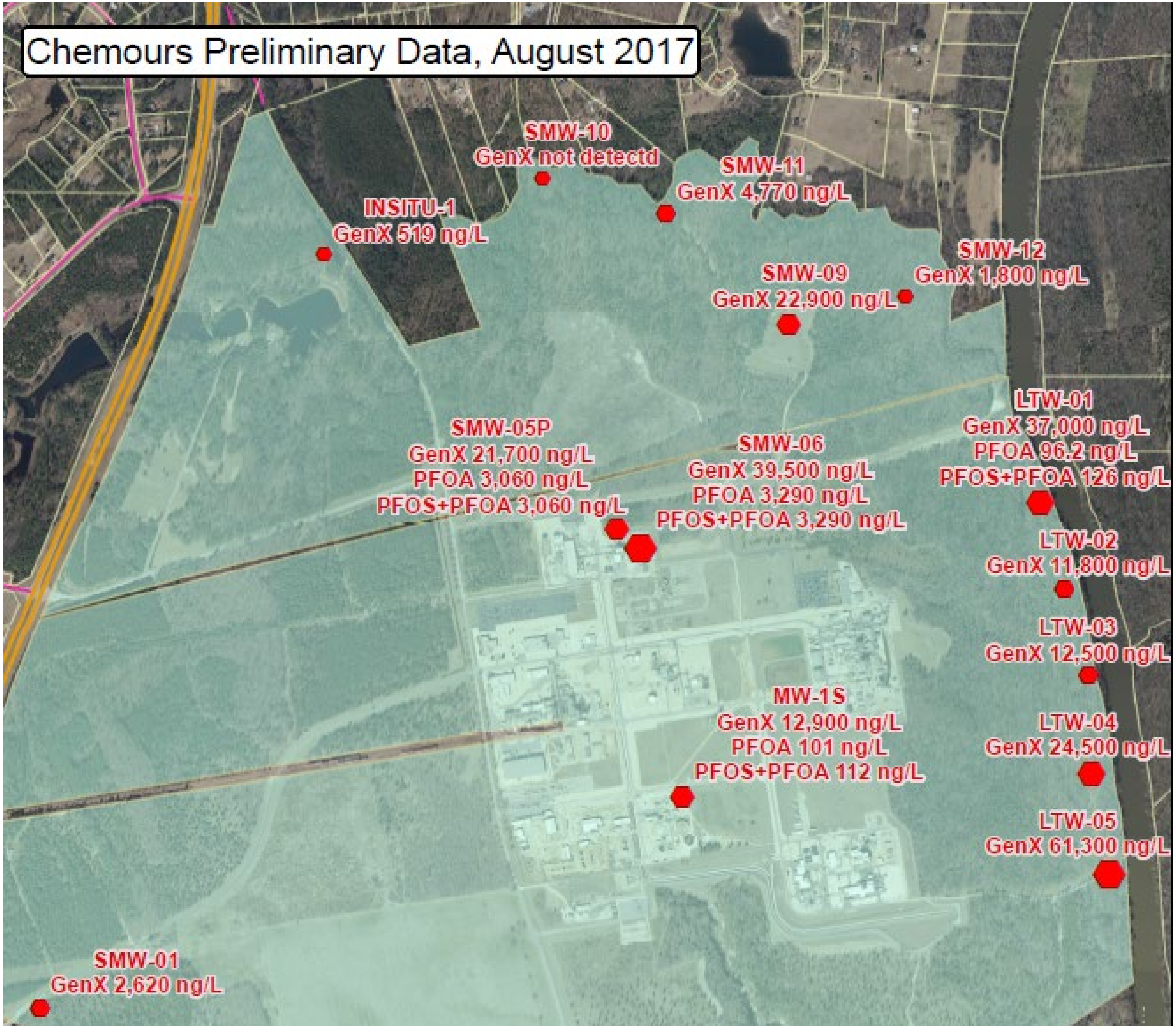
Nafion Byproduct 2

- Class: PFESAs
- Formula: $C_7H_2F_{14}O_5S$
- CAS no.: 749836-20-2
- Monoisotopic Mass : 463.9399 Da
- Ref: Strynar et al., ES&T 2015

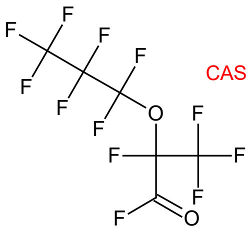


EPA Data: PFECA Concentrations in Wilmington Drinking Water (8/31/17 Data Release)



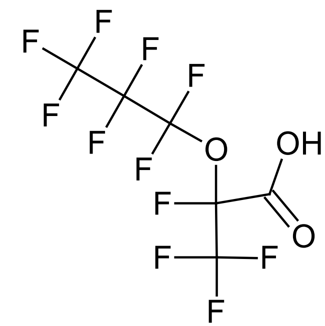

Chemours Preliminary Data, August 2017
SMW-10
GenX not detectd
SMW-11
GenX 4,770 ng/L
INSITU-1
GenX 519 ng/L
SMW-12
GenX 1,800 ng/L
SMW-09
GenX 22,900 ng/L
LTW-01
GenX 37,000 ng/L
PFOA 96.2 ng/L
PFOS+PFOA 126 ng/L
SMW-05P
GenX 21,700 ng/L
PFOA 3,060 ng/L
PFOS+PFOA 3,060 ng/L
SMW-06
GenX 39,500 ng/L
PFOA 3,290 ng/L
PFOS+PFOA 3,290 ng/L
LTW-02
GenX 11,800 ng/L
LTW-03
GenX 12,500 ng/L
MW-1S
GenX 12,900 ng/L
PFOA 101 ng/L
PFOS+PFOA 112 ng/L
LTW-04
GenX 24,500 ng/L
LTW-05
GenX 61,300 ng/L
SMW-01
GenX 2,620 ng/L

Likely Air Emission contributors to HFPO-DA detection near Chemours

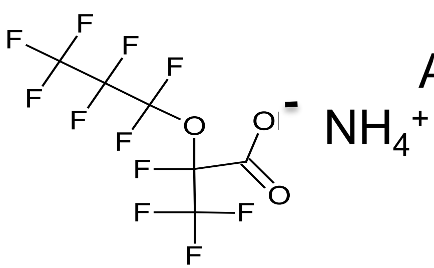


CAS 2062-98-8

Acid Fluoride – hydrolyzes to HFPO-DA



Ammonium salt– dissociates to HFPO-DA



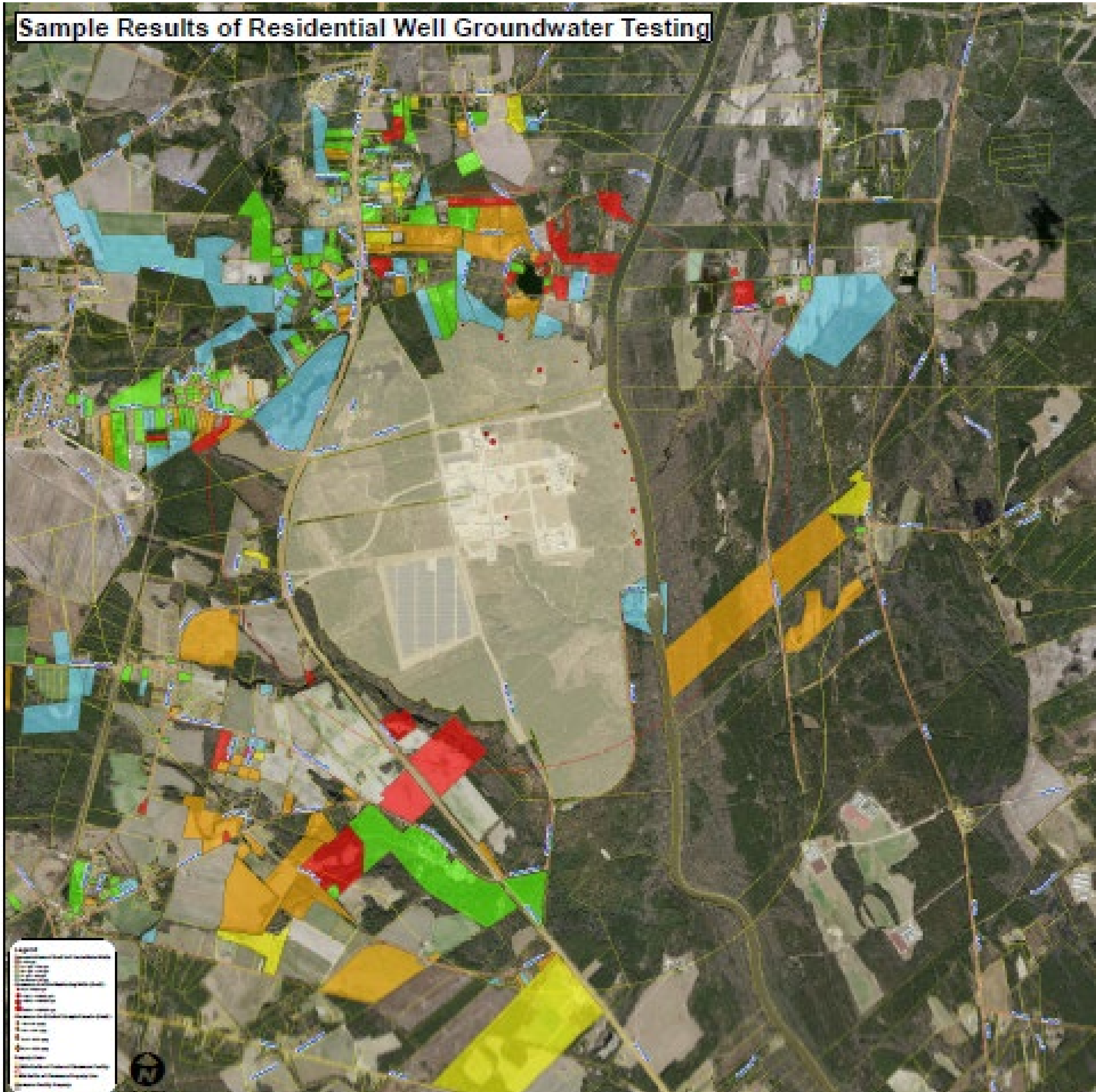
HFPO DA

CAS 13252-13-6

GenX

CAS 62037-80-3

Sample Results of Residential Well Groundwater Testing



NIH R21 Study Design

Collaborators include NCSU (Jane Hoppin, Detlef Knappe, Rob Smart, Katy May), USEPA (Mark Strynar, Andy Lindstrom), ECU (Jamie DeWitt, David Collier, Suzanne Lea)

Study population to be 100 adult males, 100 adult females, 100 boys (age 6-17) and 100 girls (age 6 -17)

Water samples collected at each household, study participants to provide blood, urine, and questionnaire data on water consumption patterns

Analysis of blood, urine, and water will be done at NERL by NCSU students under the direction of EPA

Chemical analysis will focus on legacy PFAS, replacement compounds documented in the Sun et al. 2016 paper + Nafion byproducts, and NTA assessment

Questions?

Email: lindstrom.andrew@epa.gov